

**Interim Report on Task 1.2: Near Equilibrium Processing  
Requirements**

**Part 2 of 2**

**APPENDICES**

**To Lawrence Livermore National Laboratory for Contract  
B345772**

M W A Stewart, E R Vance, R A Day and A Brownscombe

April 5, 1999

*U.S. Department of Energy*

Lawrence  
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National  
Laboratory

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R99m012

# **Interim Report on Task 1.2: Near Equilibrium Processing Requirements**

## **Appendices**

### **To Lawrence Livermore National Laboratory for Contract B345772**

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**Stewart, Vance, Day  
Brownscombe**

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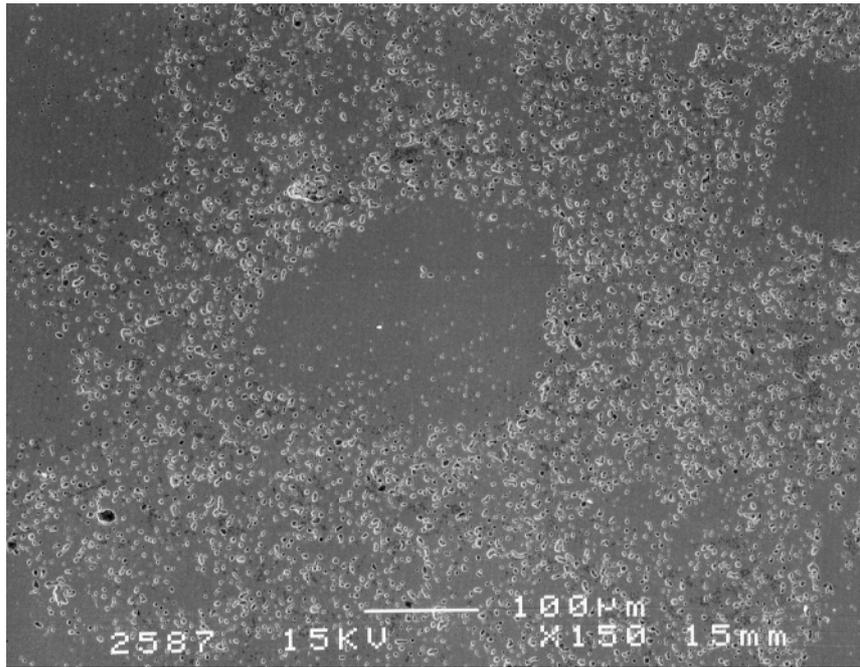
**E R Vance**

Australian Nuclear Science and Technology Organisation  
Postal Address: Private Mail Bag 1, Menai, NSW 2234, Australia  
Materials Division: Telephone +61 2 9717 3265 • Facsimile +61 2 9543 7179

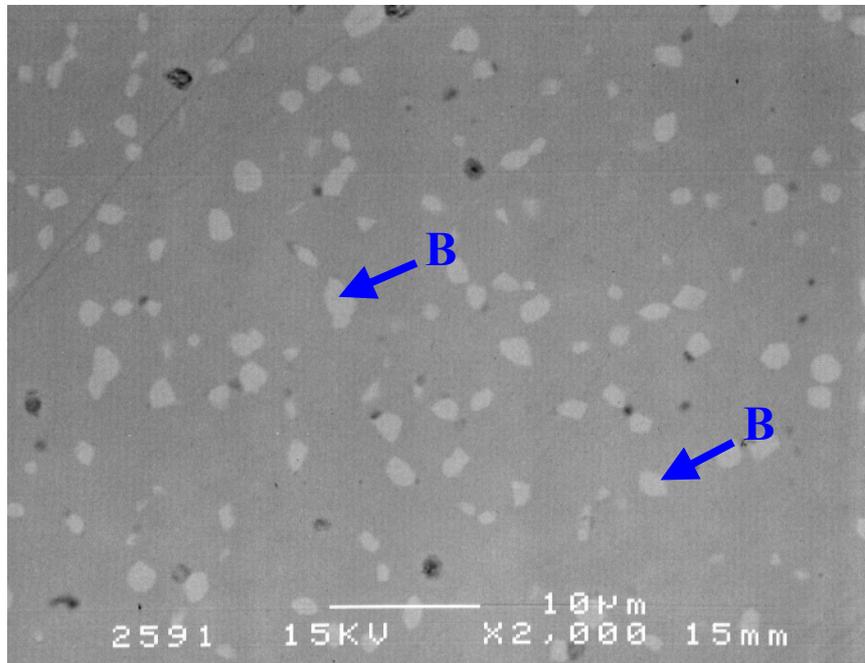
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# **APPENDIX A**

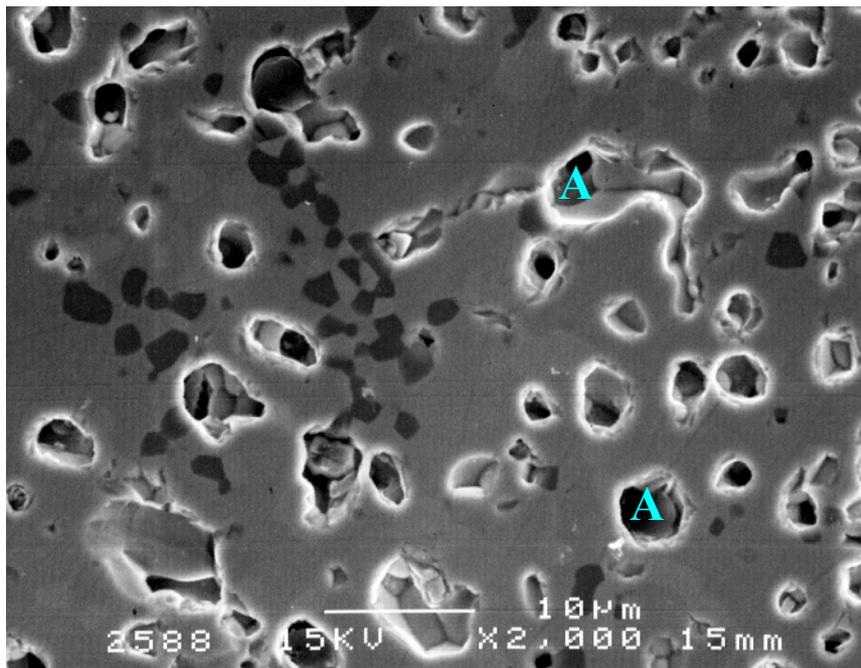
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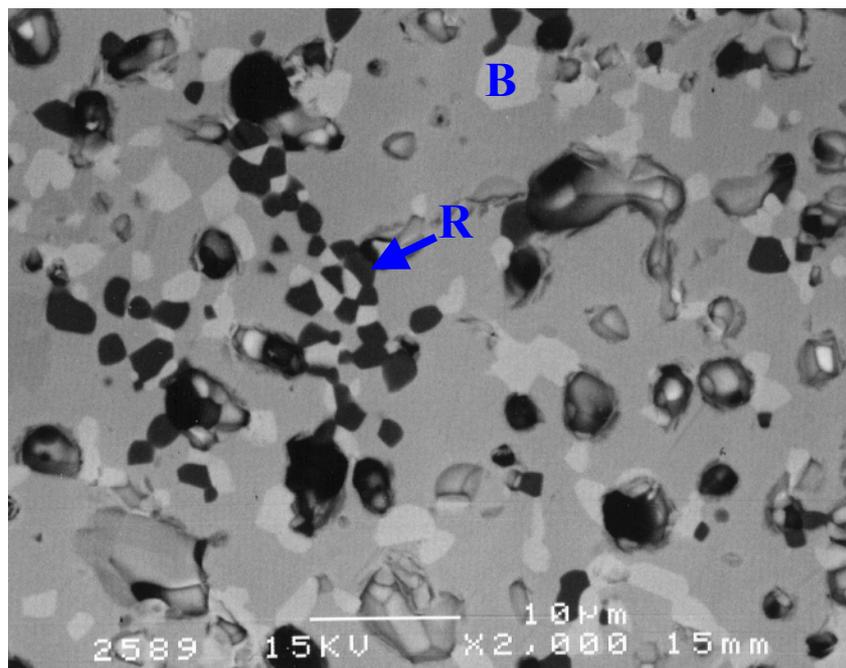
(a)  100 µm.



(b)  10 µm.

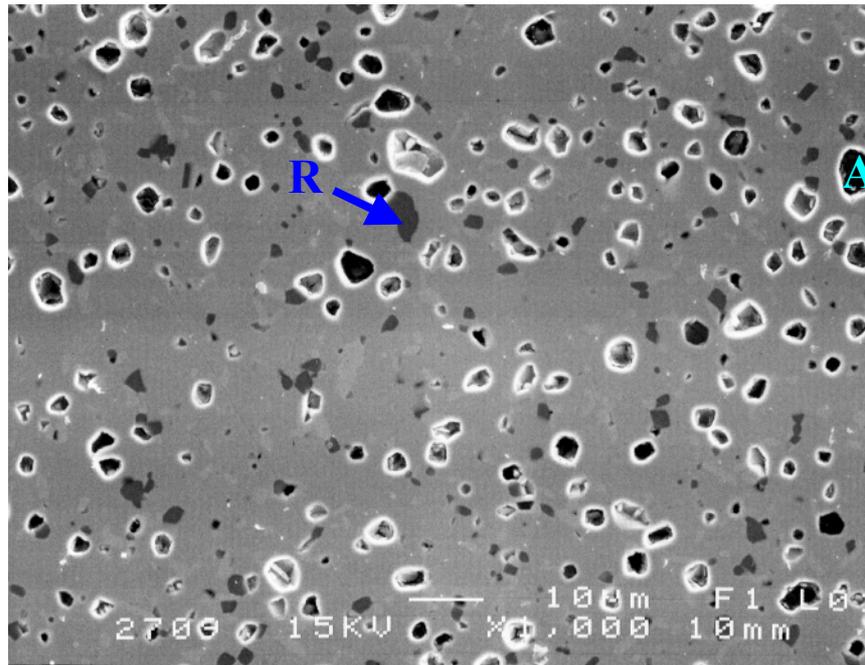


(c)

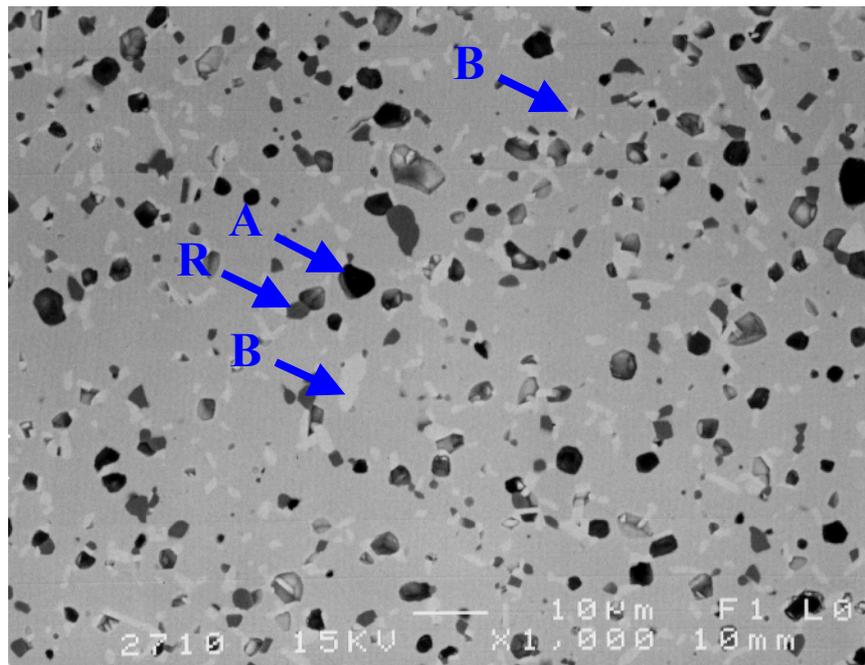


(d)  10 μm.

Figure C-1: Micrographs of mws980106 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 4 hours, sintered at 1350°C in Ar for 4 hours). (a) Secondary electron micrograph of overall microstructure showing that the sample has dense and porous regions. (b) backscattered electron micrograph of the dense region; this region consists of a pyrochlore matrix and Th/U-brannerite (B, light grey grains). (c) Secondary electron micrograph and (d) backscattered electron micrograph of the porous region. This porous region consists of a pyrochlore matrix with Th/U-brannerite (B, light grey grains). Hf-doped rutile (R, dark-grey) and porosity (A) are also present

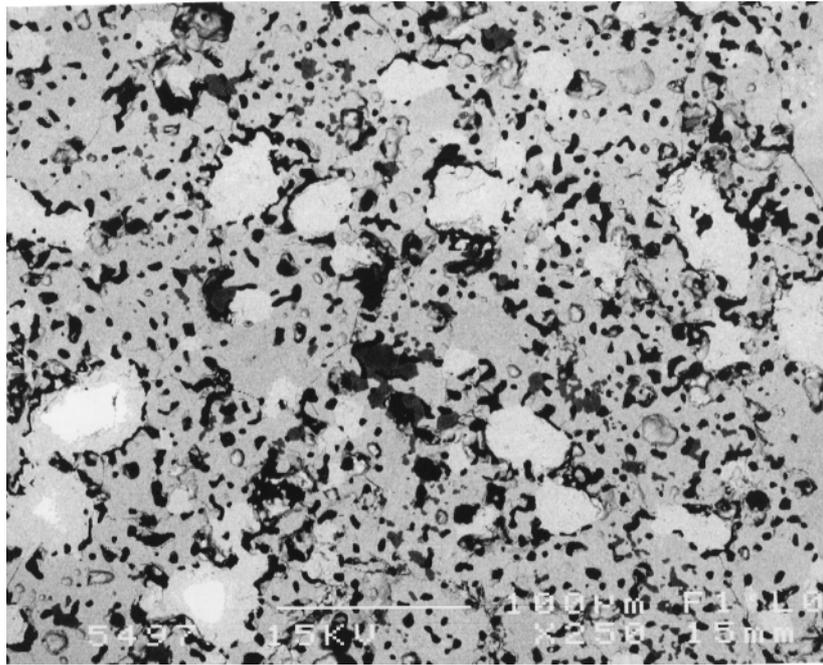


(a)

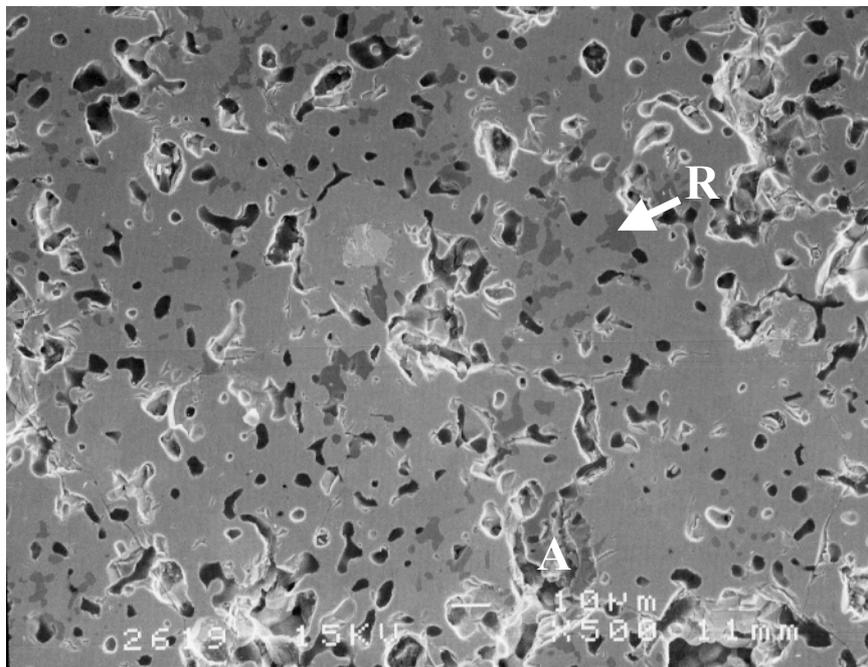


(b) — 10  $\mu\text{m}$ .

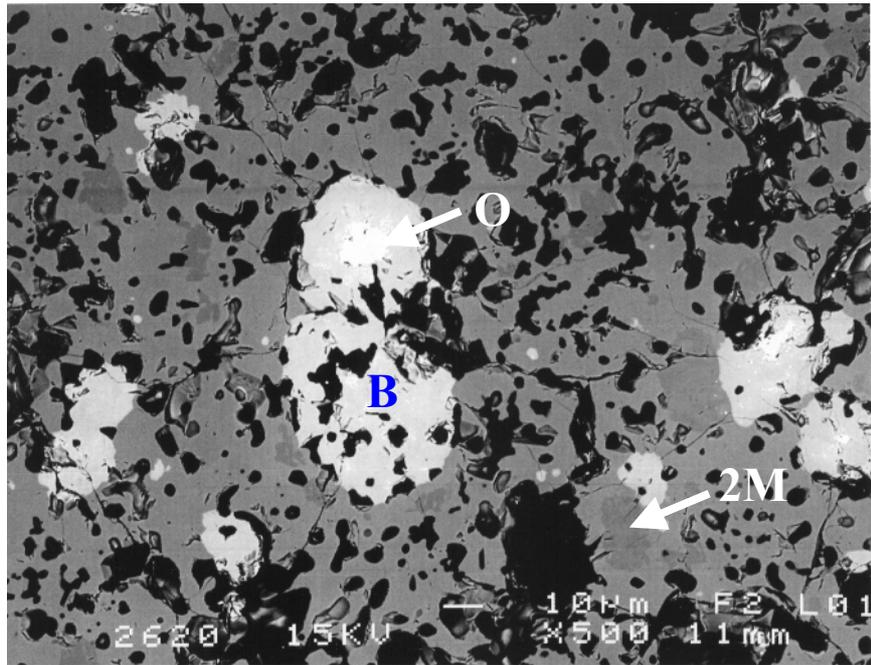
Figure C-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980173 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey) and porosity (A) are present.



(a)  100 μm.

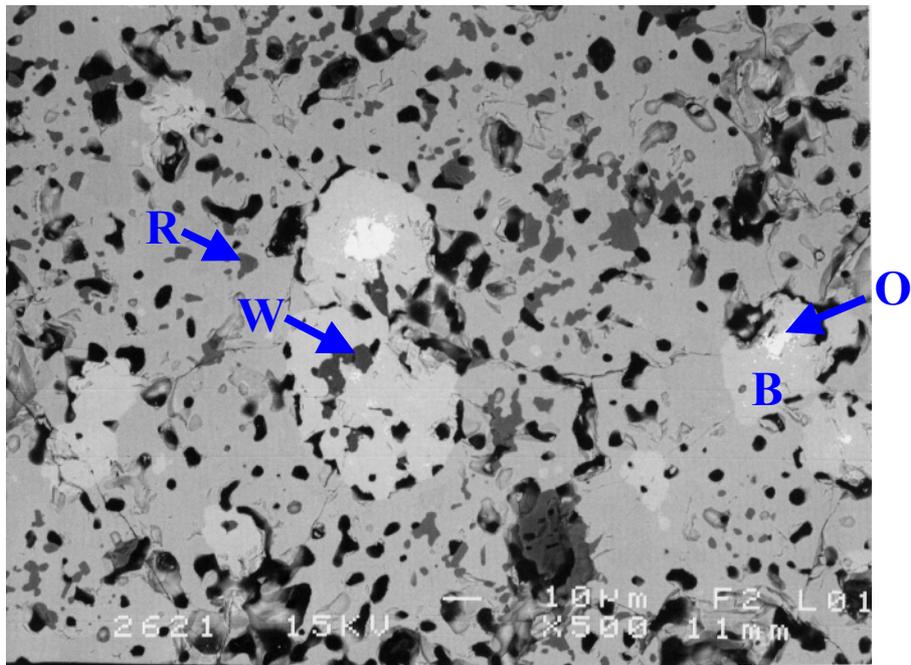


(b)  10 μm.



(c)

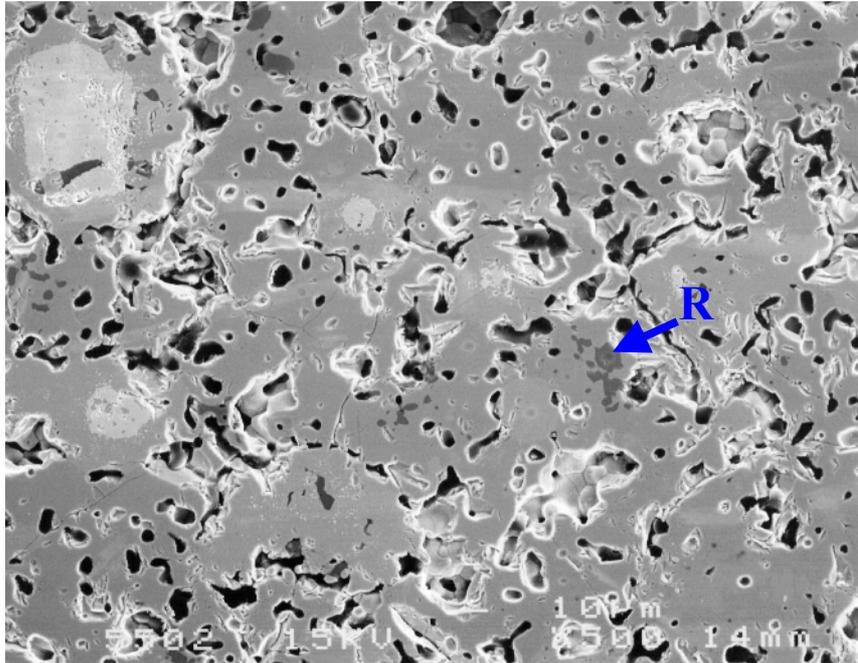
— 10 µm.



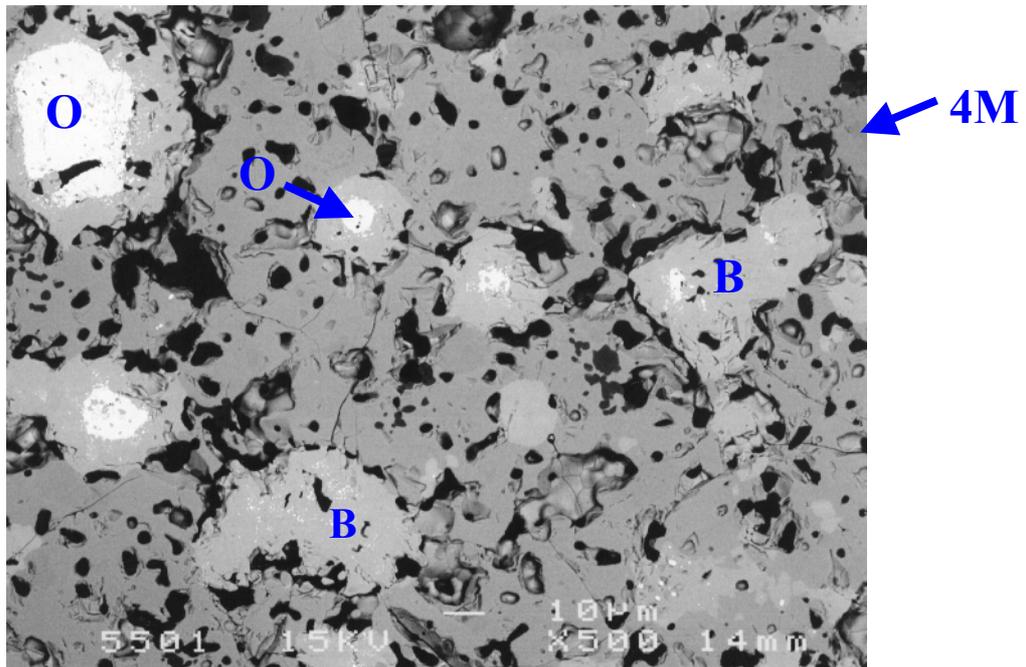
(d)

— 10 µm.

Figure C-3: Micrographs of mws980134 Task 1.2, composition B1-2, oxide-route, dry-milled 4 hours, sintered at 1350°C in Ar for 4 hours. (a) Backscattered electron micrograph at low magnification illustrates the inhomogeneity in the sample. (b) Secondary electron micrograph and, (b) and (d) backscattered electron micrographs at differing contrasts of a region the sample. The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), 2M zirconolite (2M), ThO<sub>2</sub> (O, white), a trace of whitlockite (W) and porosity (A) are present.



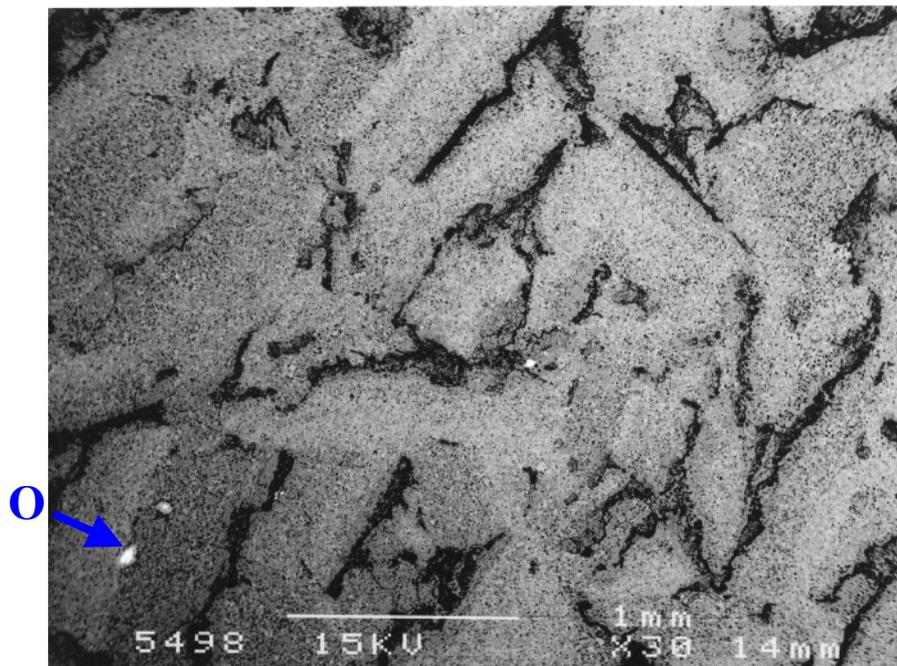
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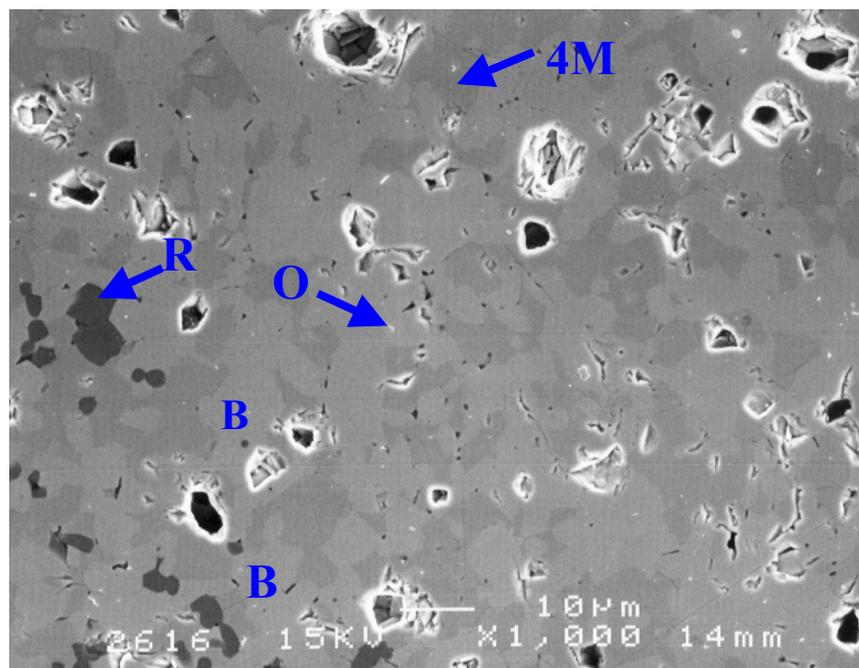
(b)

— 10 µm.

Figure C-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980139 (Task 1.2, composition B1-2, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), 4M zirconolite (4M), unreacted ThO<sub>2</sub> (O, white) surrounded by brannerite and porosity (see (a)) are present.



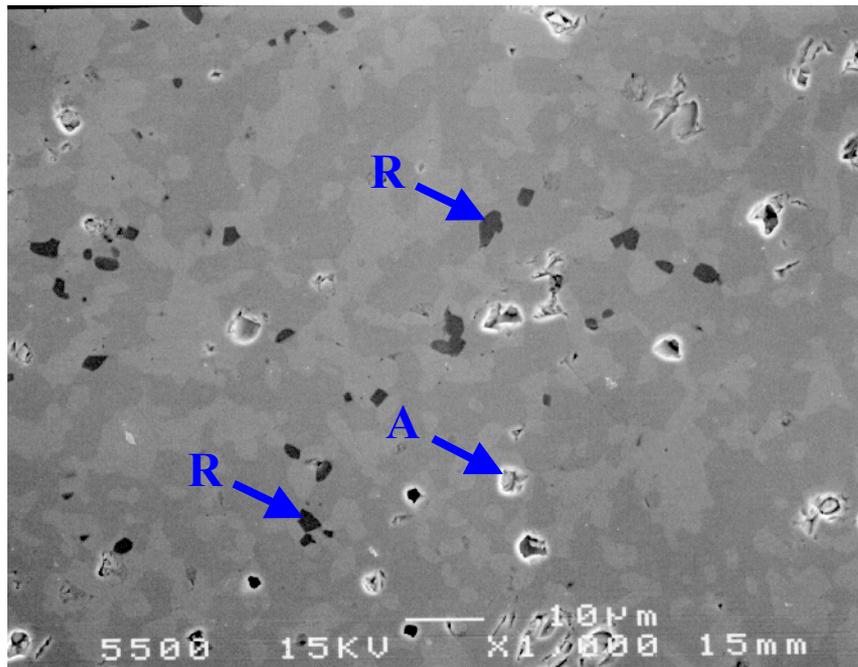
(a)



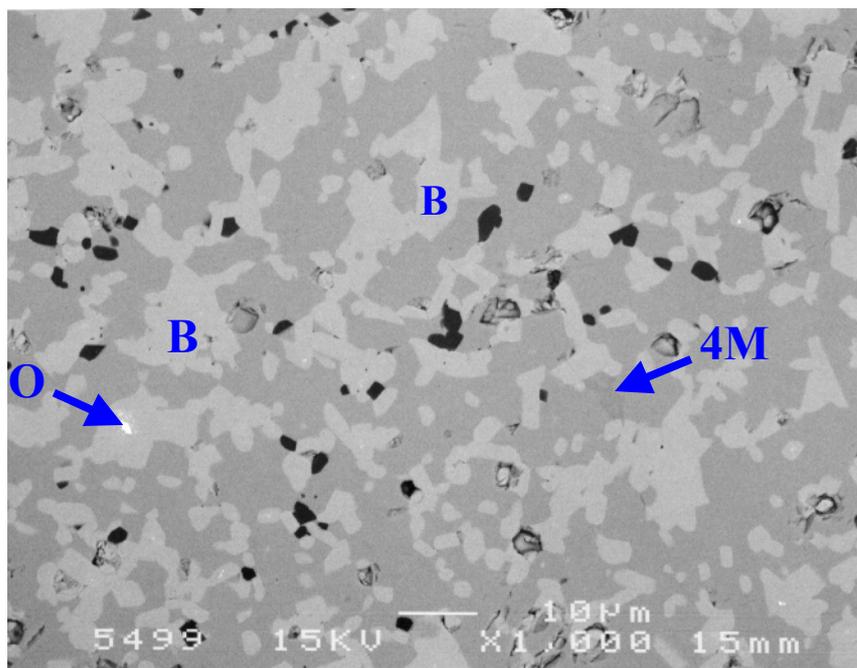
(b)

— 10 µm.

Figure C-5: (a) Backscattered electron micrograph at low magnification and (b) backscattered electron micrograph at higher magnification, of mws980133 (Task 1.2, composition B1-2, oxide-route, wet-milled 4 hours, sintered at 1350°C in Ar for 4 hours). The sample contains mm sized lumps, with some variation in composition across the sample. The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), 4M zirconolite (4M), ThO<sub>2</sub> (O, white) and porosity (A) are present.



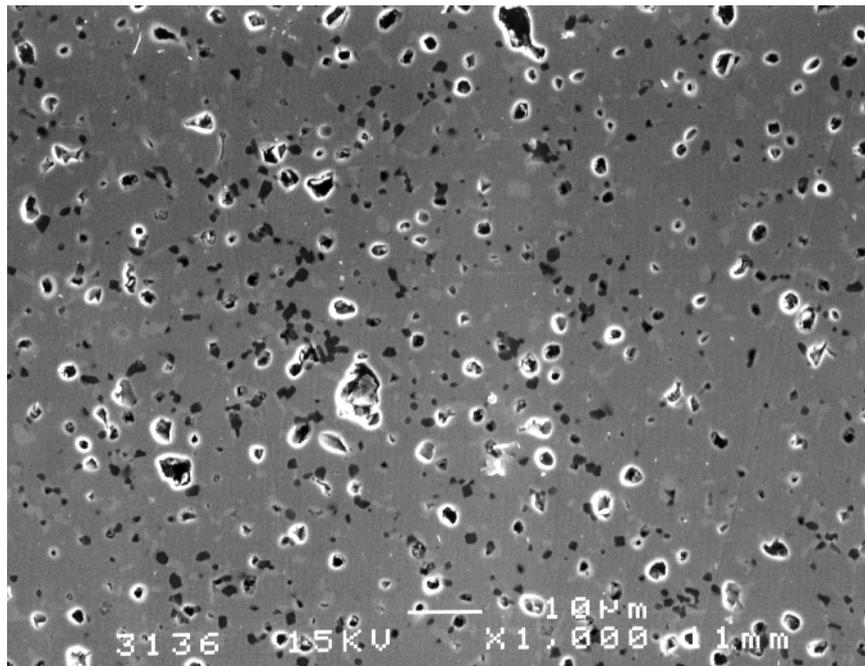
(a)



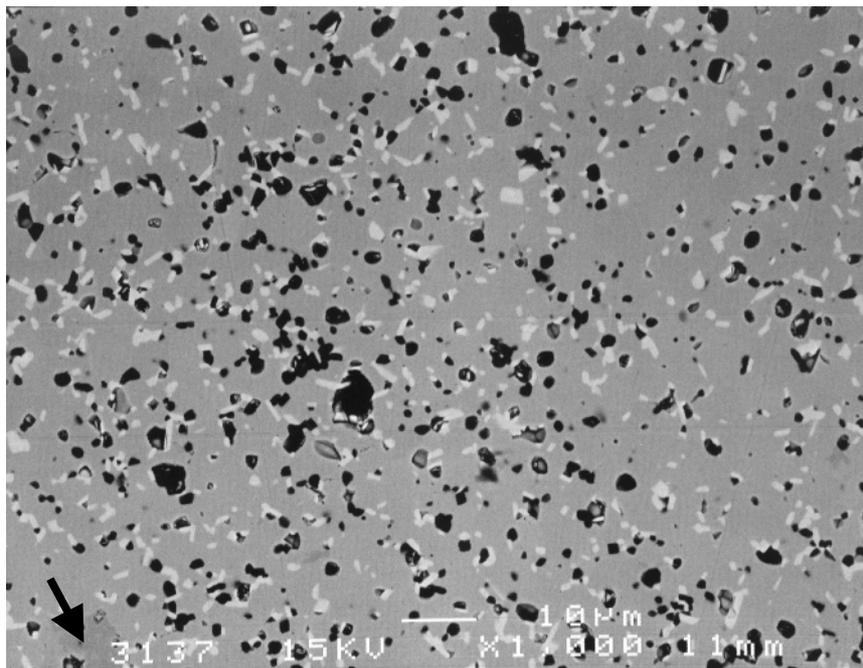
(b)

— 10 µm.

Figure C-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980137 (Task 1.2, composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), 4M zirconolite (4M), ThO<sub>2</sub> (O, white) and porosity (A) are present.



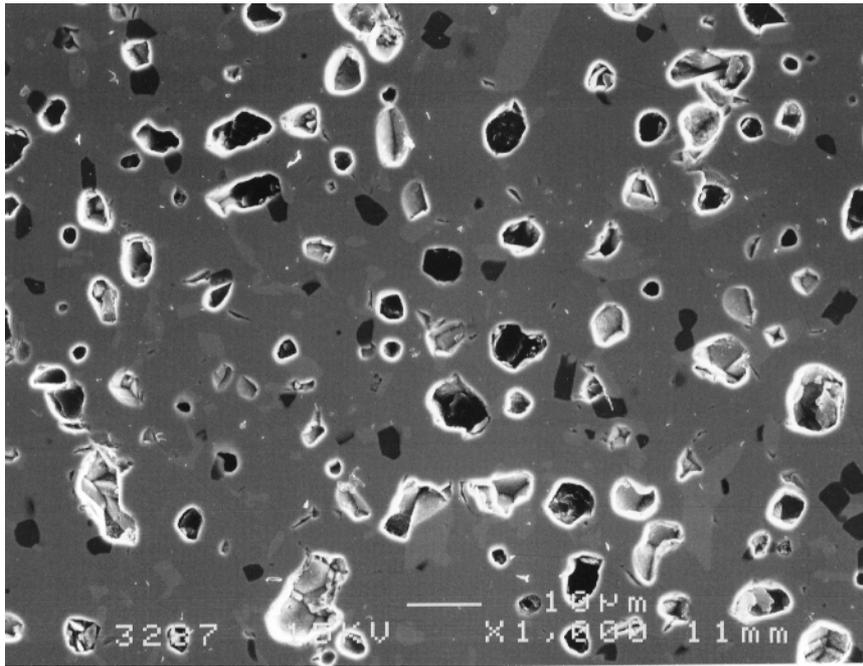
(a)



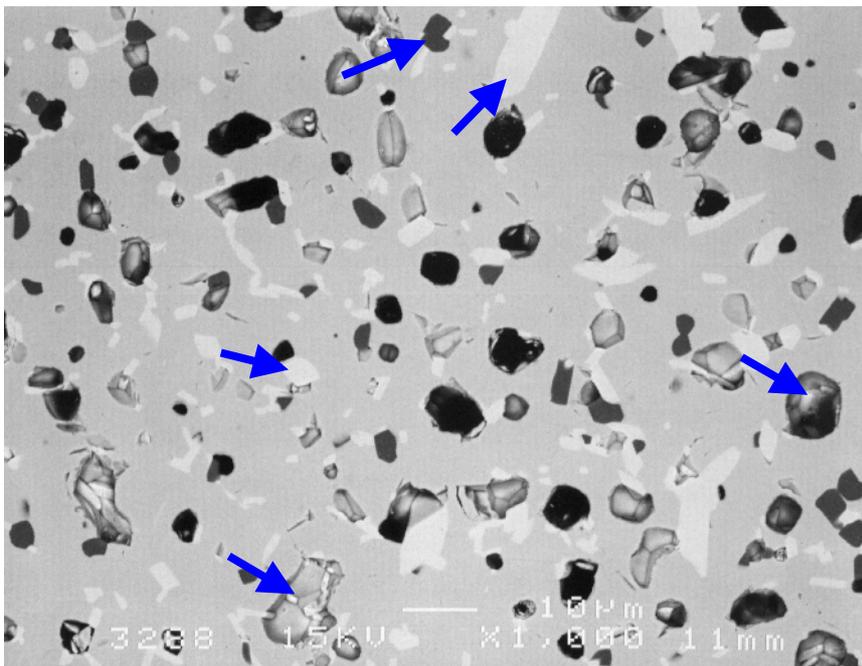
(b)

— 10  $\mu\text{m}$ .

Figure C-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980309 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The matrix is pyrochlore, the light-grey phase is Th/U-brannerite and the dark-grey phase is Hf-bearing rutile. Some 4M zirconolite can be seen in (b) – regions that are slightly darker than the matrix, e.g., at the bottom of the micrograph (see arrow). Porosity is also present and can be seen in (a).

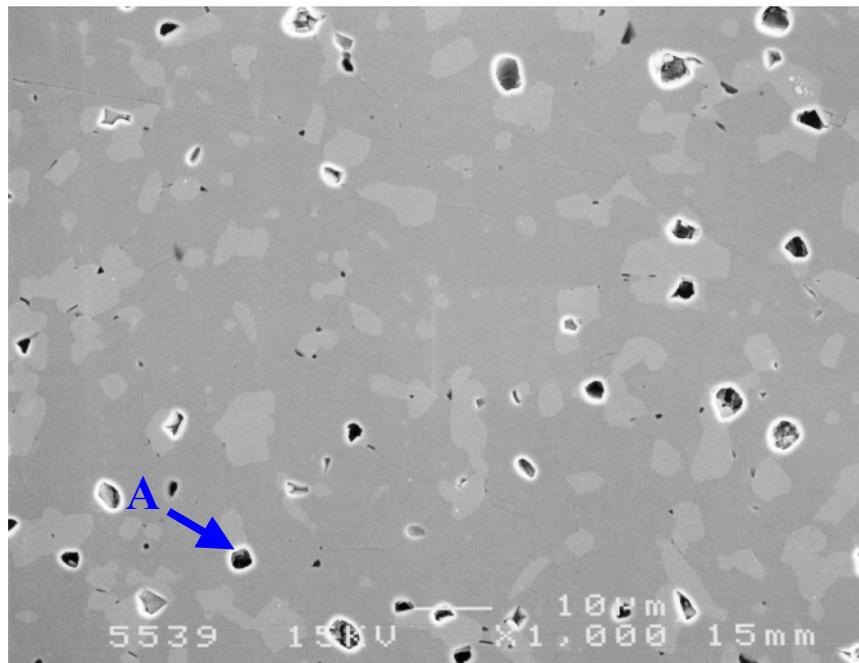


(a) — 10 μm.

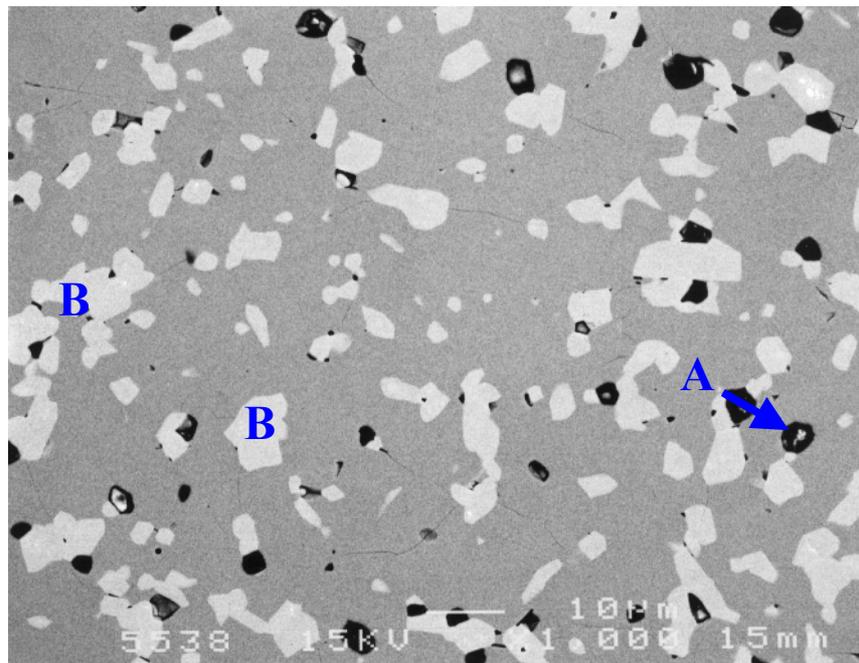


(b) — 10 μm.

Figure C-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980323 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is pyrochlore, with brannerite (B, light grey grains) and Hf-doped rutile (R, dark-grey grains). Porosity (A) is present.

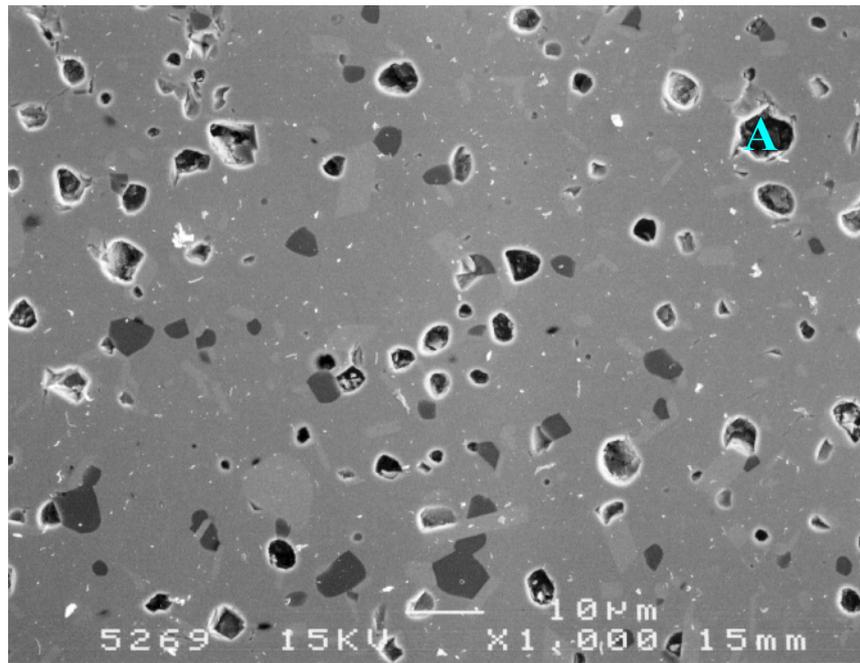


(a)

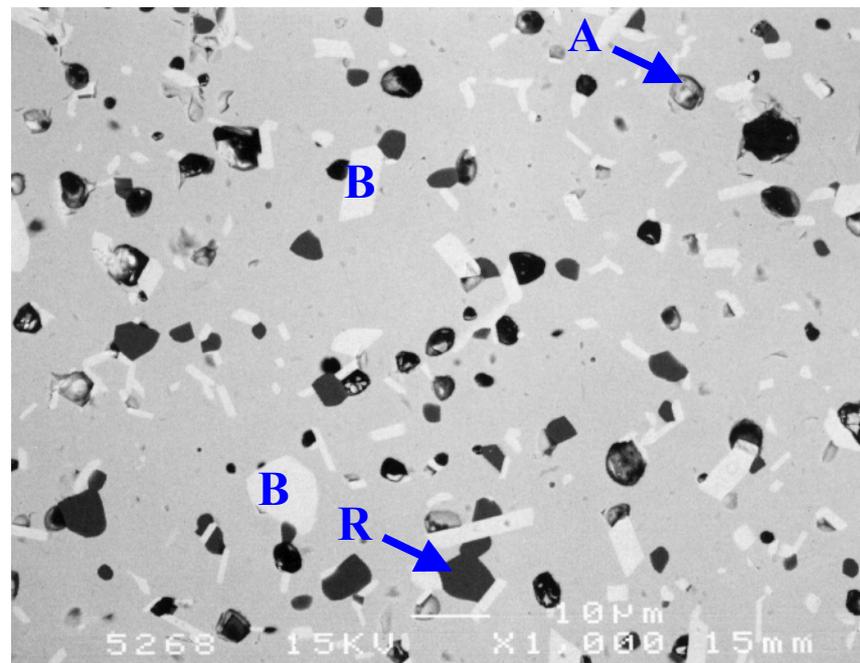


(b) — 10 µm.

Figure C-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980408 (Task 1.2, composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is pyrochlore, with brannerite (B, light grey grains) and porosity (A) present.



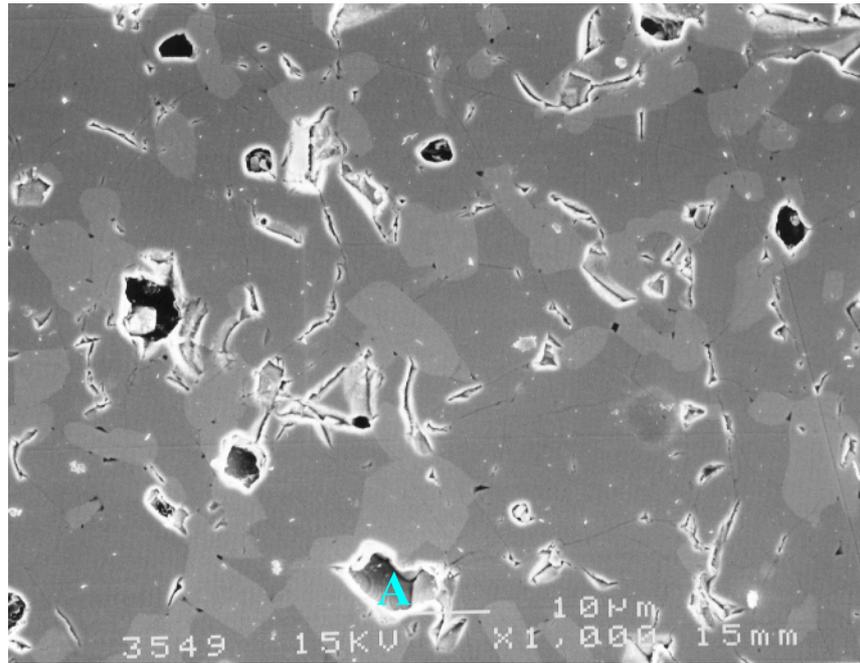
(a)



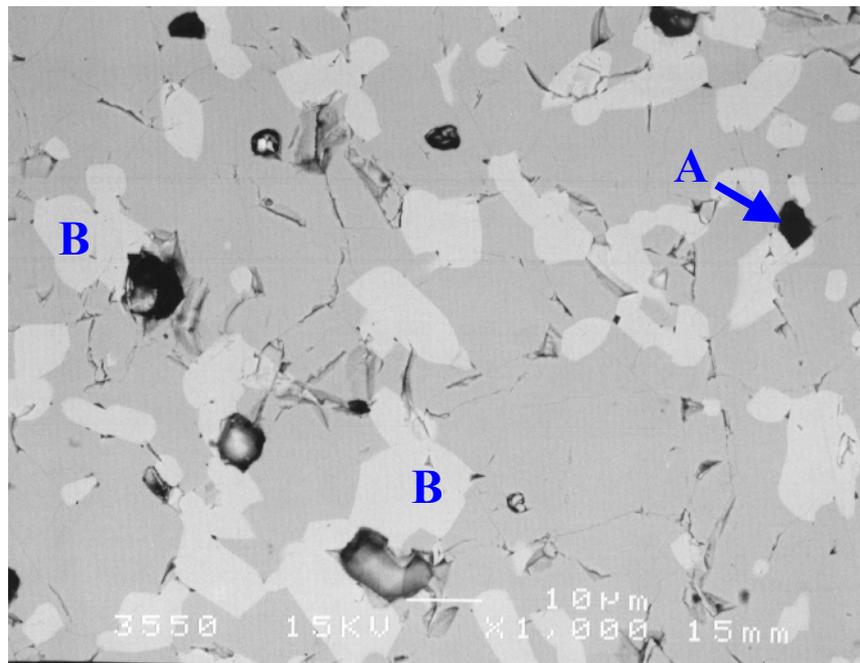
(b)

— 10 µm.

Figure C-10: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980348 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey) and porosity (A) are present.



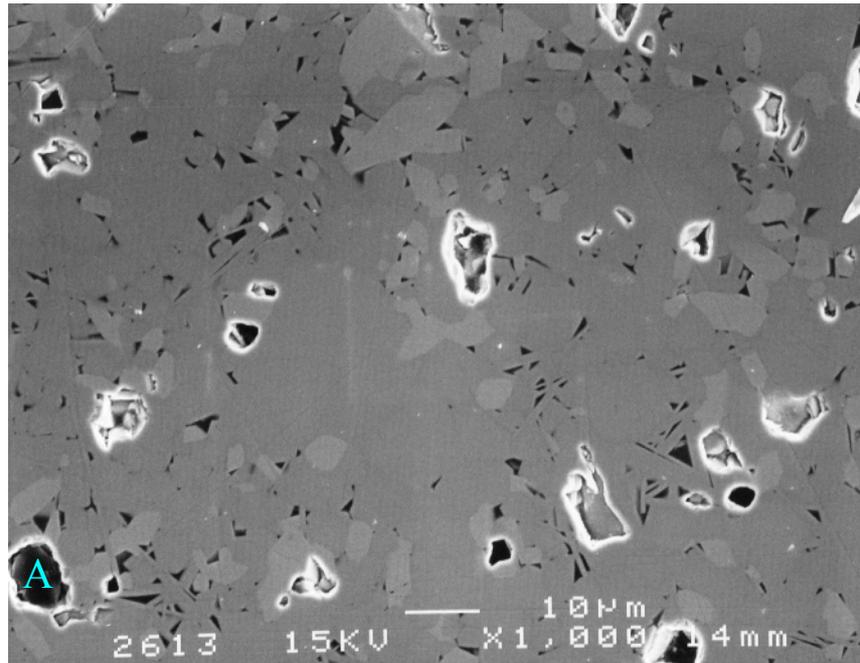
(a)



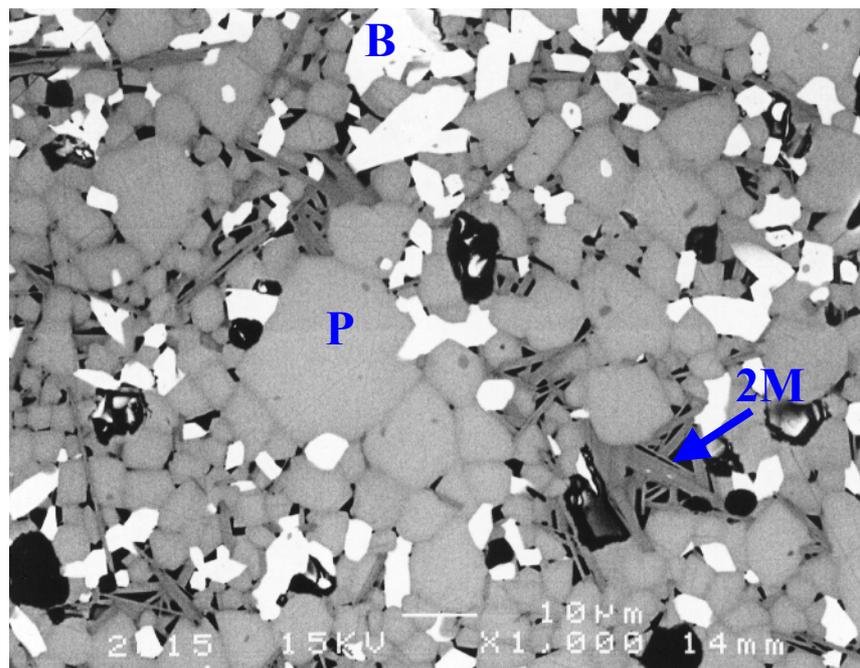
(b)

— 10 µm.

Figure C-11: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980391 (Task 1.2, composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is pyrochlore, with brannerite (B, light grey grains) and porosity (A) present.



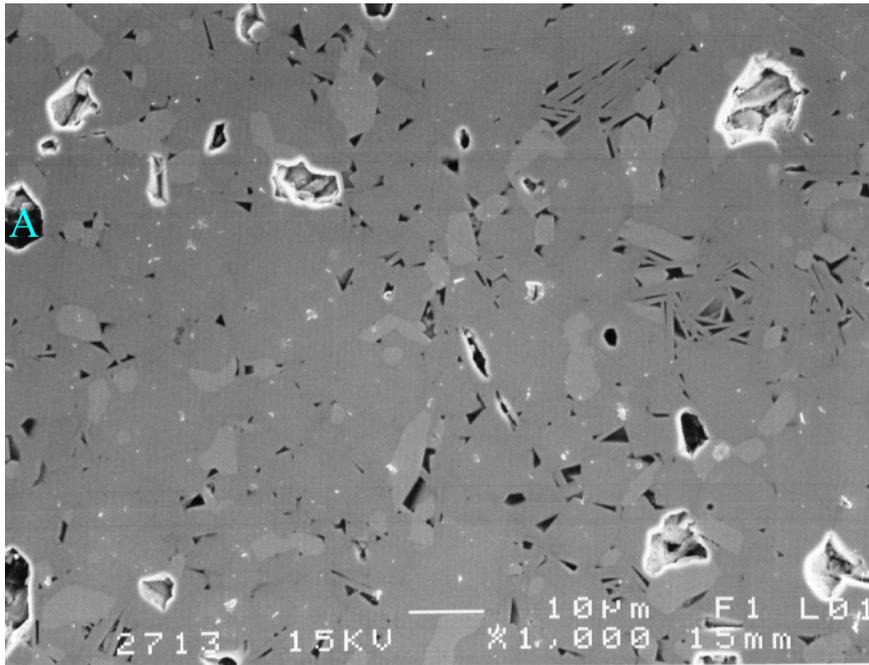
(a)



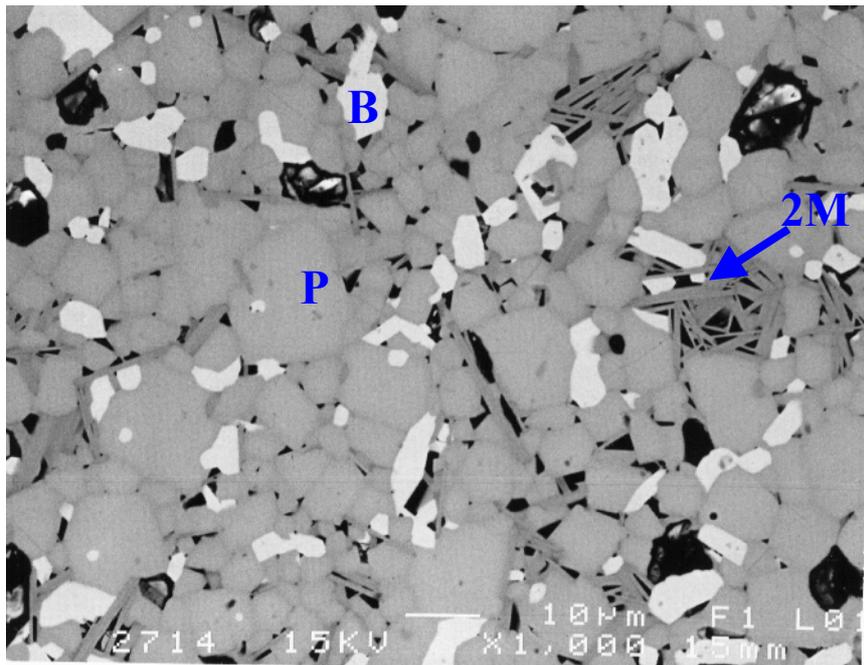
(b)

— 10 μm.

Figure D-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980112 (Task 1.2, composition B1-4, alkoxide-route, wet-milled 4 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



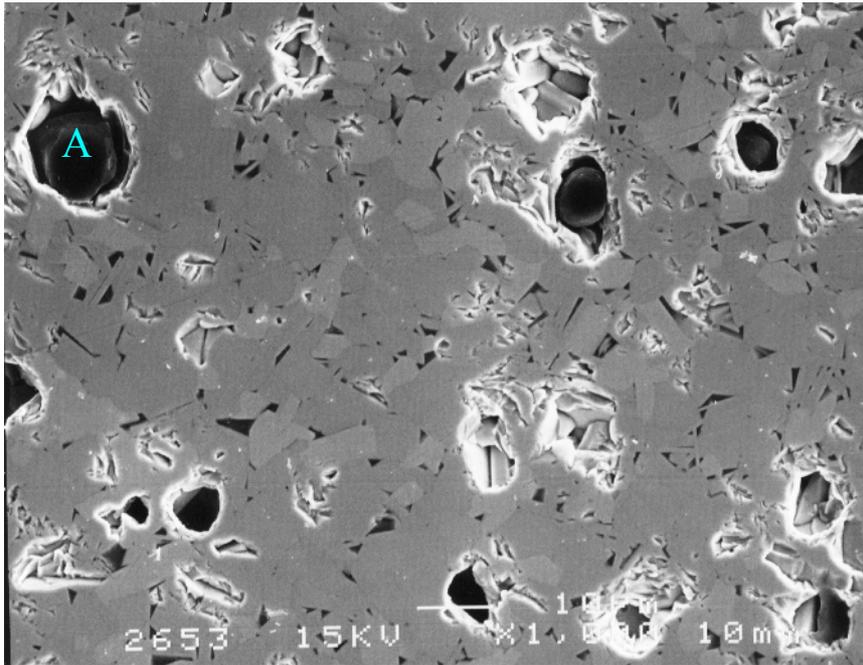
(a)



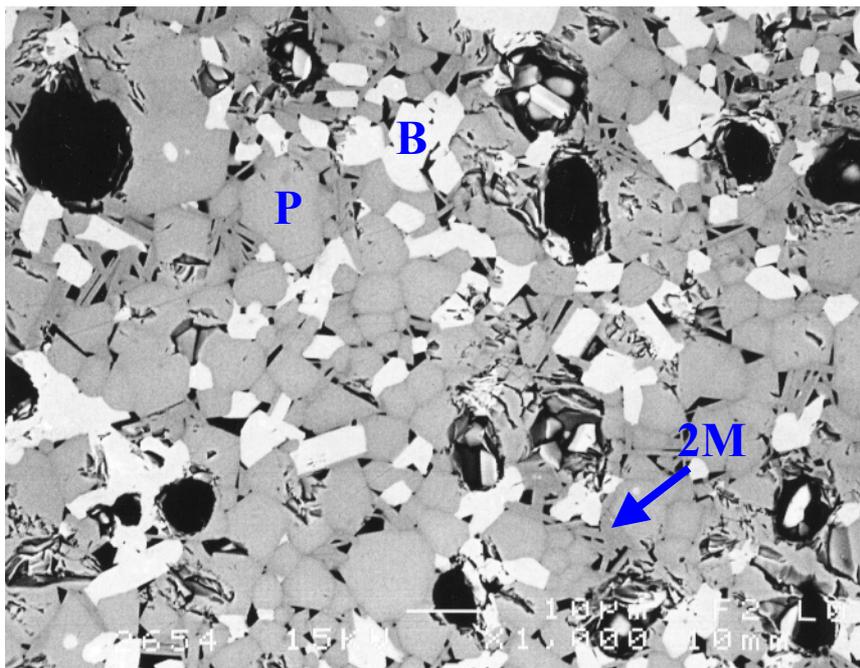
(b)

— 10 µm.

Figure D-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980177 (Task 1.2, composition B1-4, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



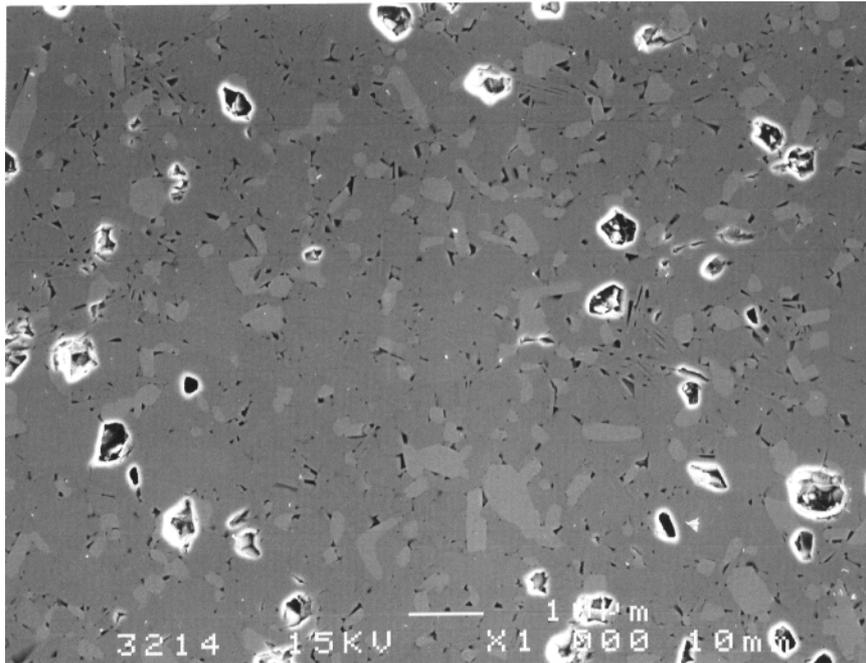
(a)



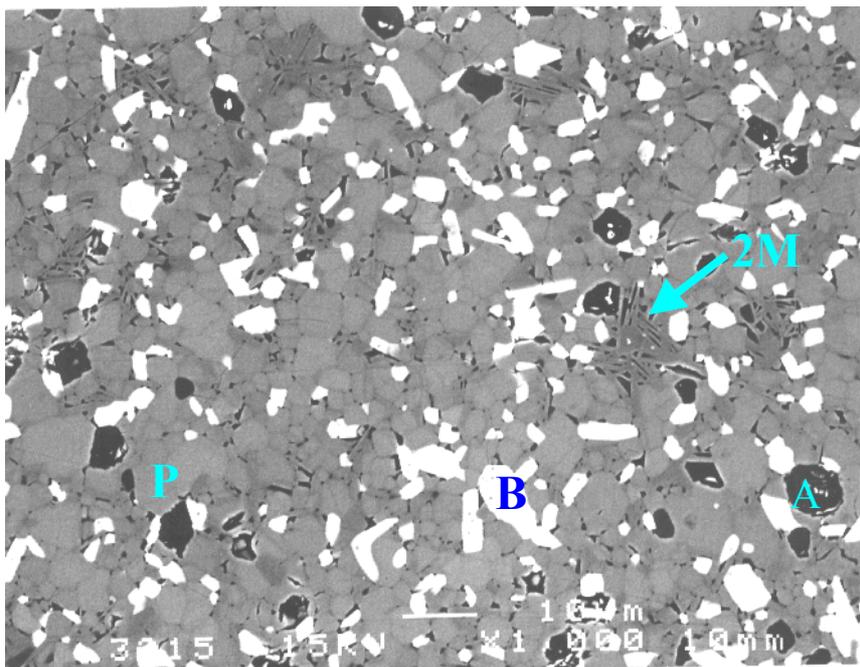
(b)

— 10 µm.

Figure D-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980151 (Task 1.2, composition B1-4, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



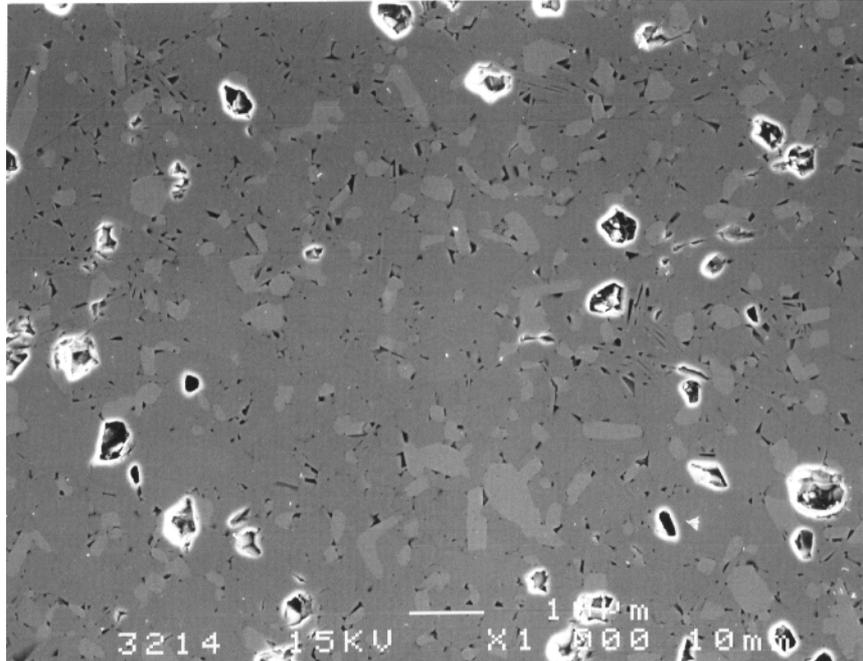
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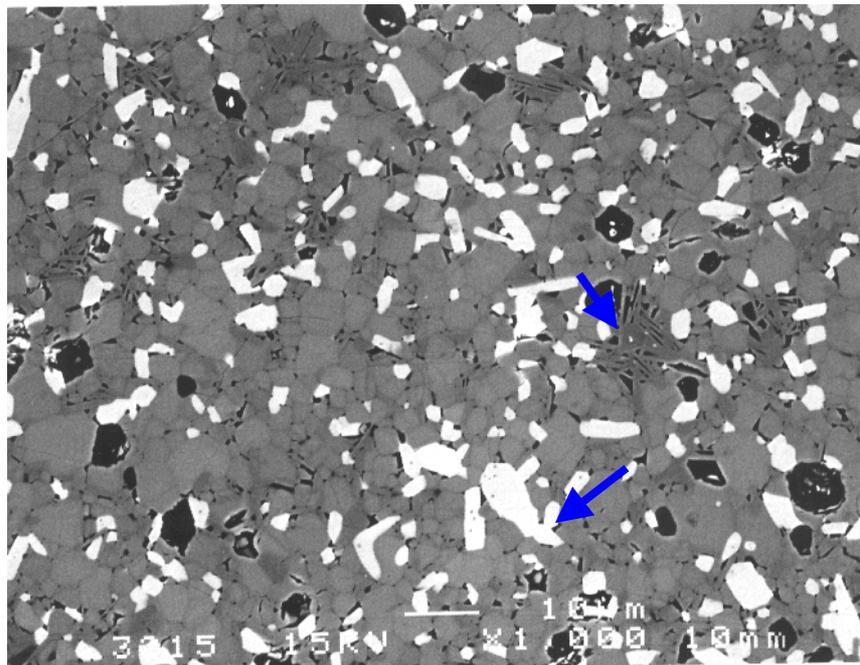
(b)

— 10 μm.

Figure D-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980149 (Task 1.2, composition B1-4, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



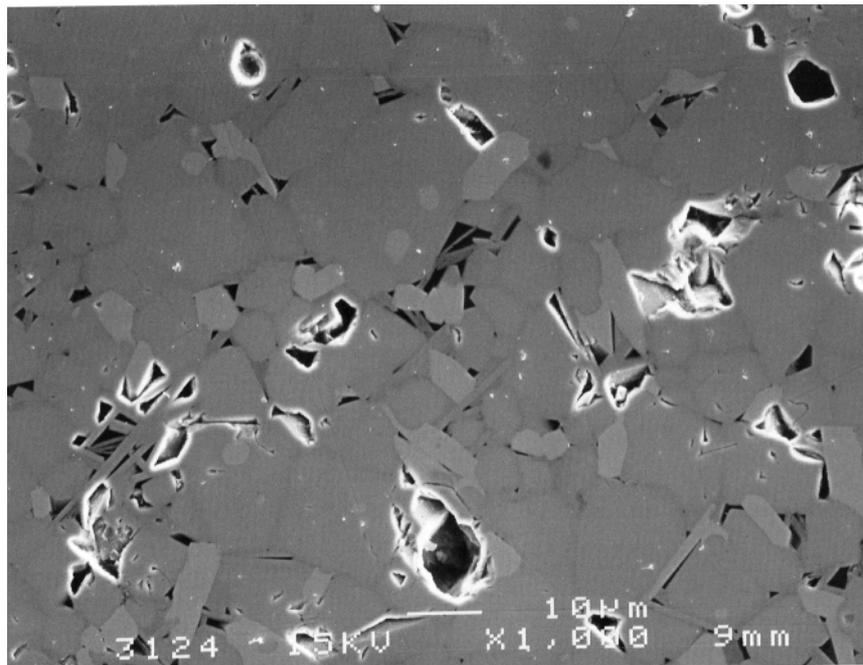
(a)



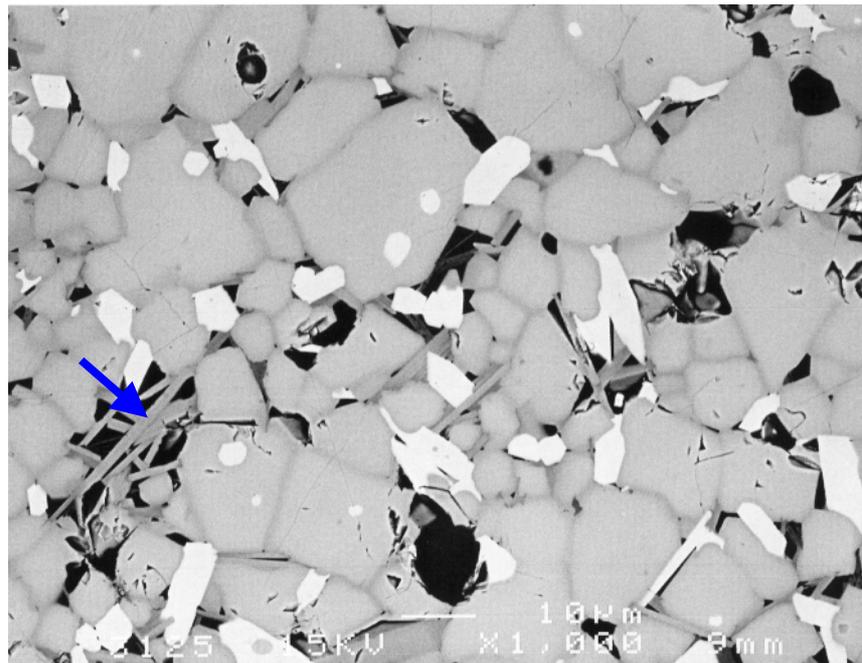
(b)

— 10 μm.

Figure D-5: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980317 (Task 1.2, composition B1-4, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The matrix is pyrochlore (P), the light grey phase is Th/U-brannerite (B) and elongated grains are 2M zirconolite (2M). Some unreacted thoria (T, white spots) is present in some brannerite grains. Porosity (A) is present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



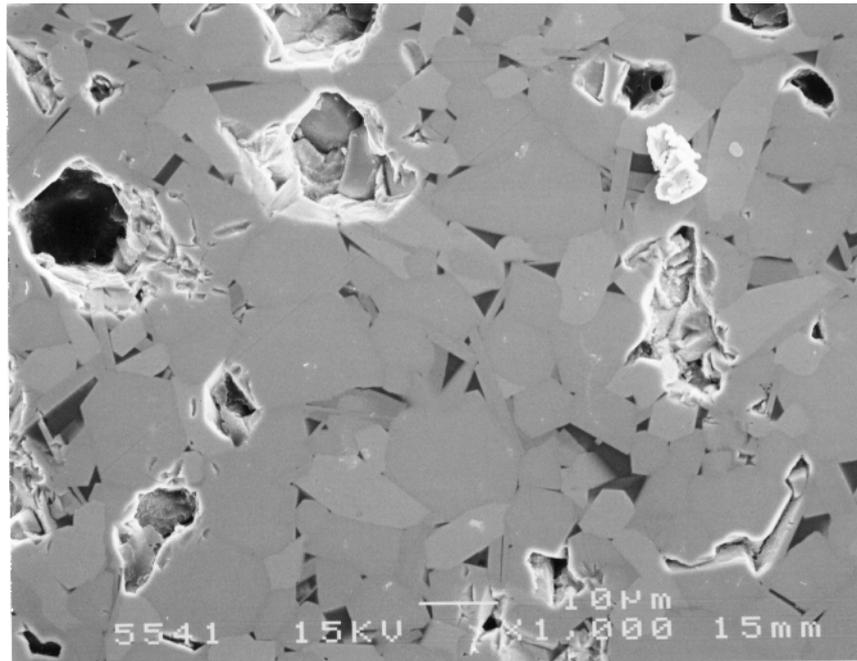
(a)



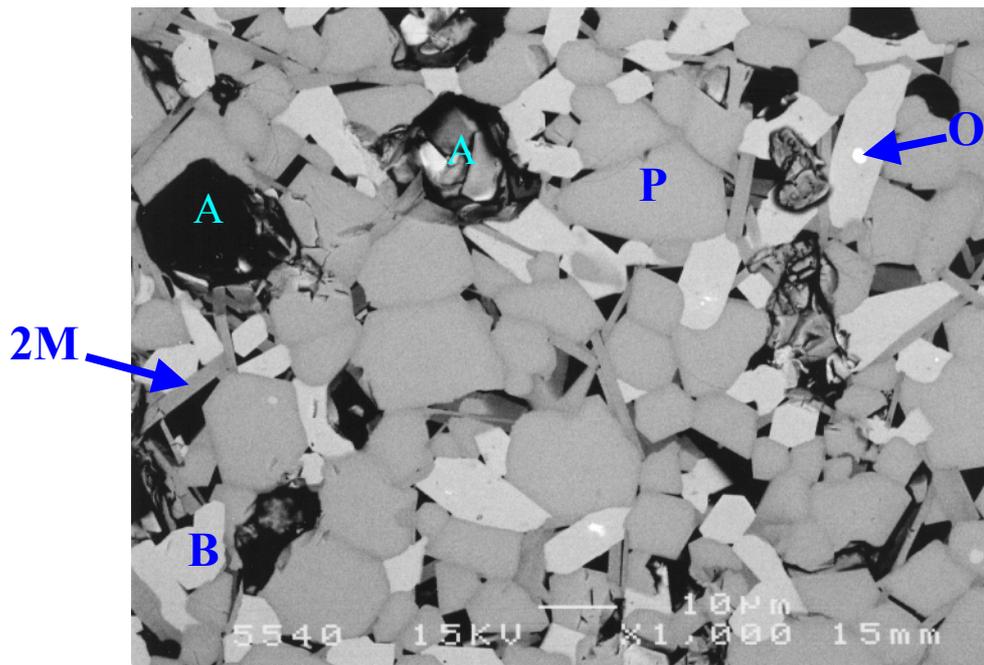
(b)

— 10 µm.

Figure D-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980303 (Task 1.2, composition B1-4, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



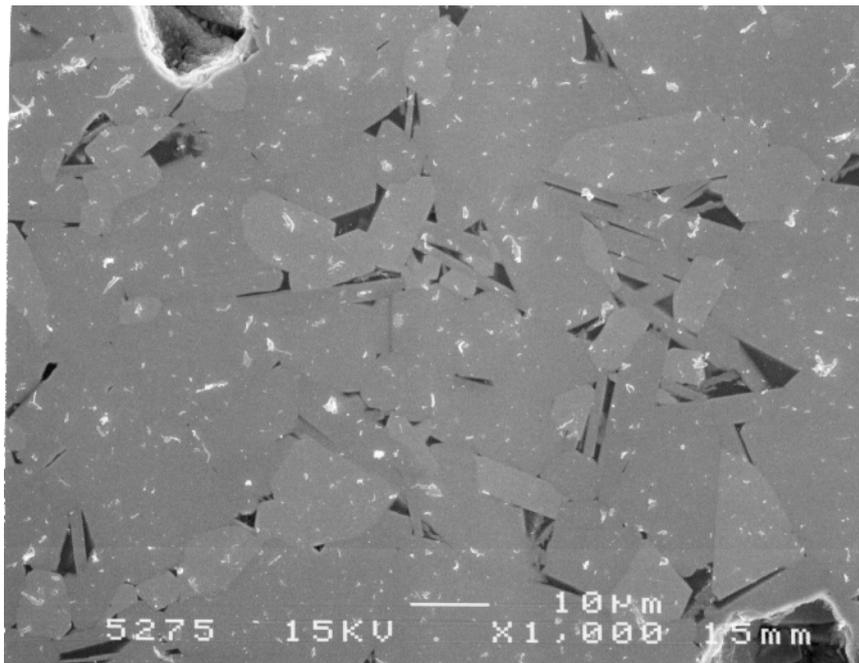
(a)



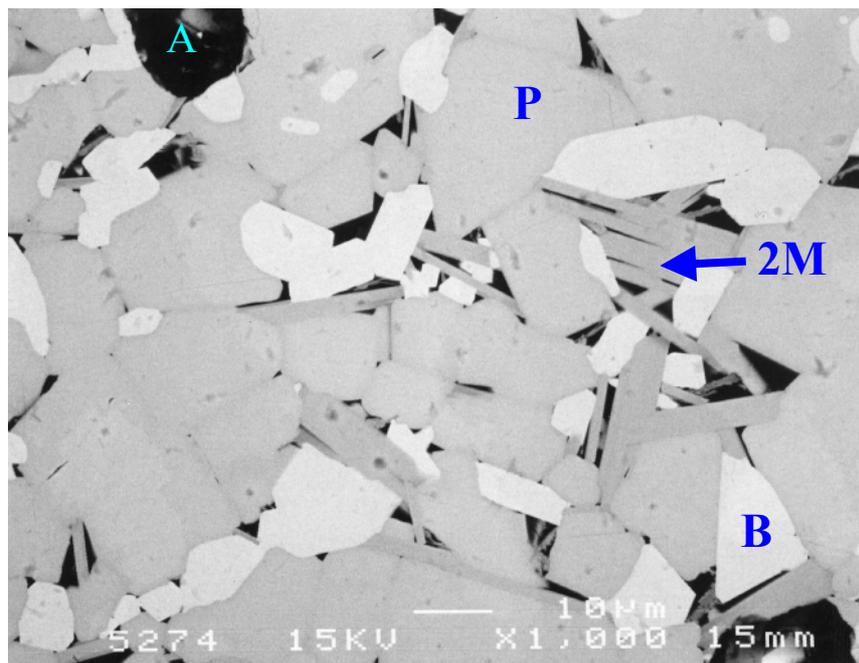
(b)

— 10 μm.

Figure D-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980408 (Task 1.2, composition B1-4, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B), the elongated grains are 2M zirconolite (2M) and the white spots inside the brannerite grains are (Th,U)O<sub>2</sub> (O). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



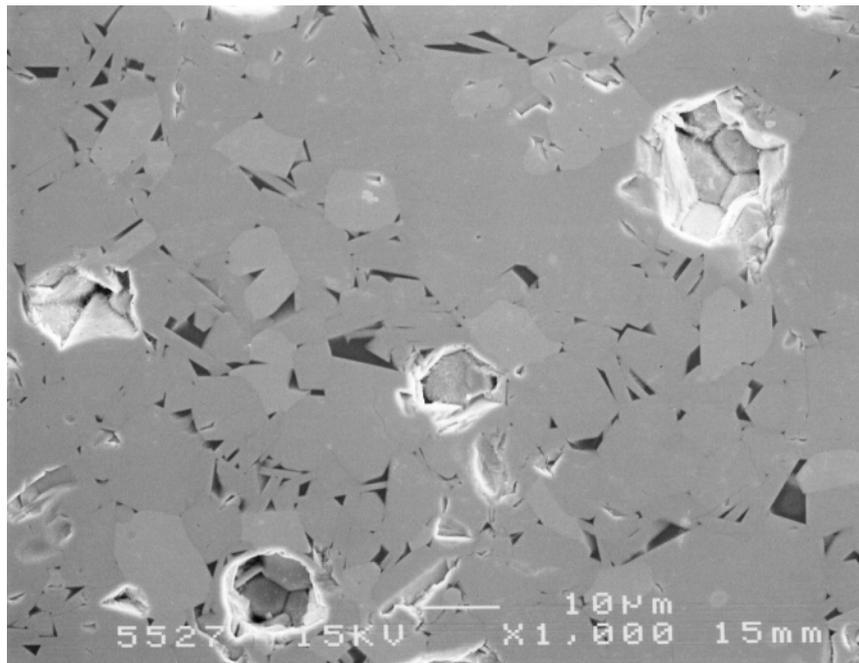
(a)



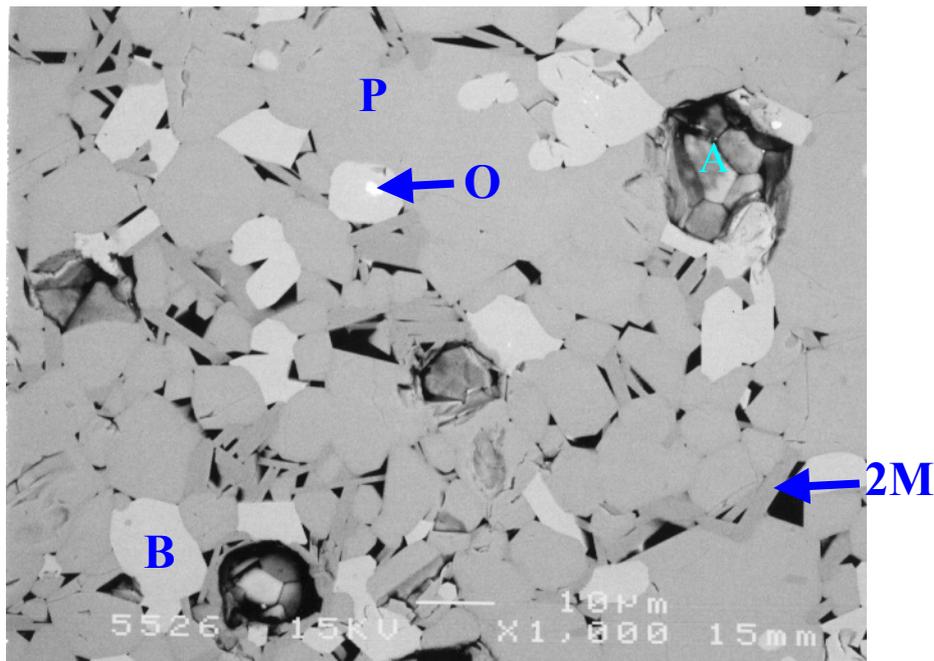
(b)

— 10 μm.

Figure D-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980351 (Task 1.2, composition B1-4, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



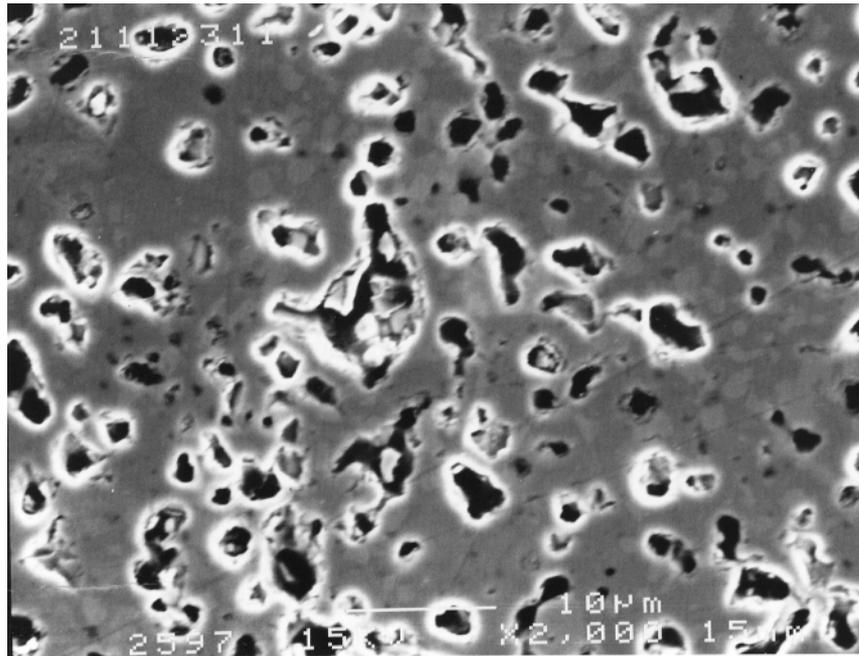
(a)



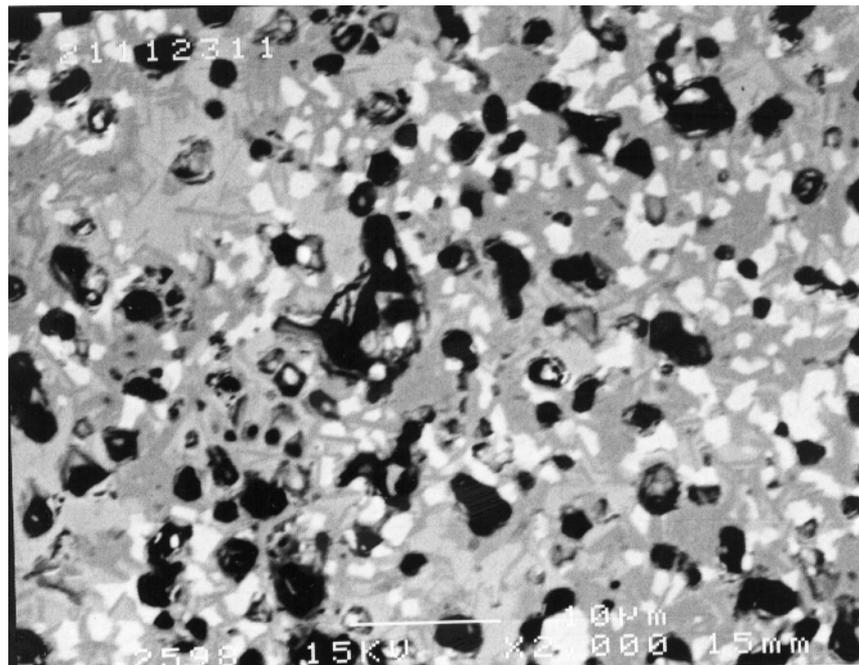
(b)

— 10 μm.

Figure D-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980394 (Task 1.2, composition B1-4, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). ThO<sub>2</sub> (O, white) can be seen inside some of the brannerite grains. Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



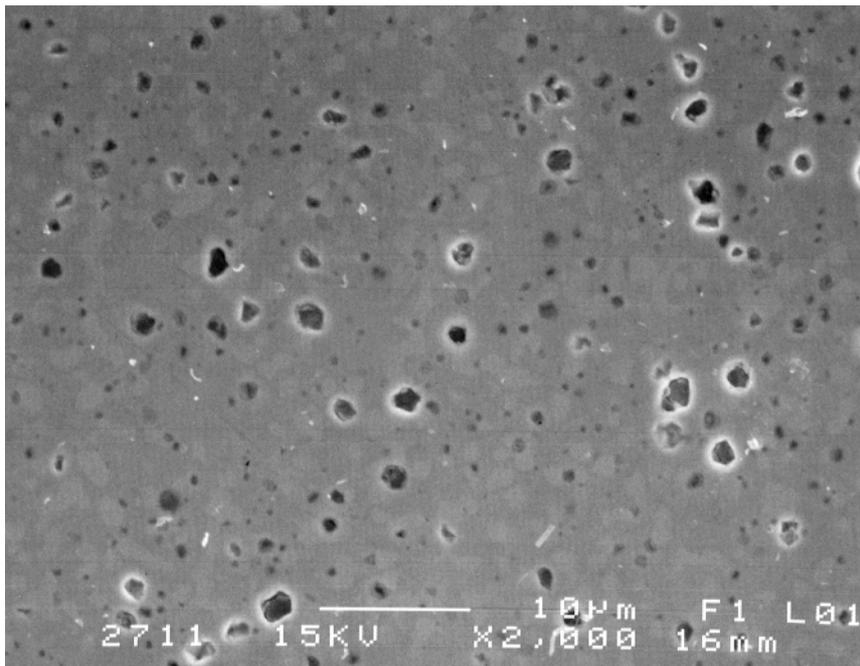
(a)



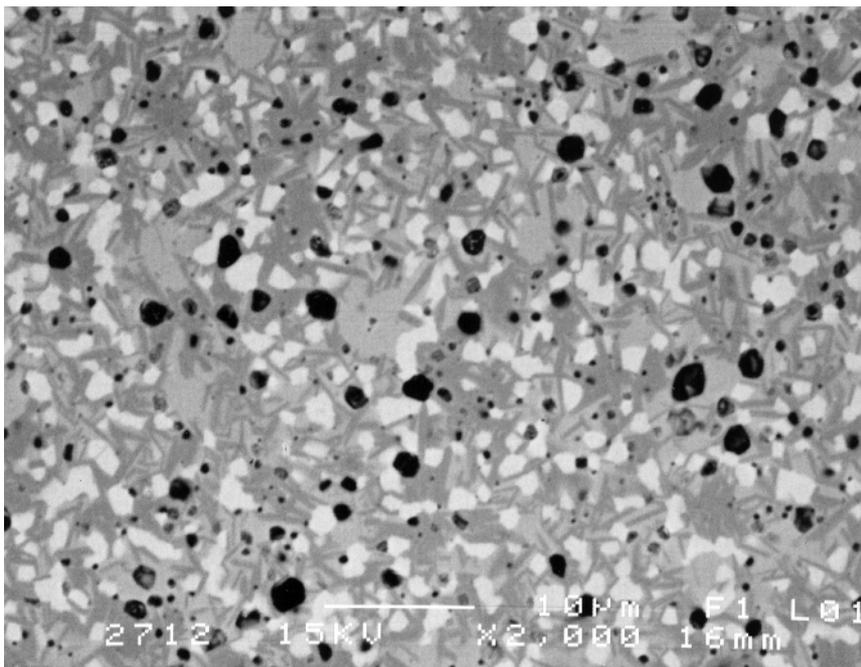
(b)

— 10 µm.

Figure E-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980108 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 4 hours, sintered at 1350°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix), the light-grey phase is Th/U-brannerite and porosity (see (a)) is also present.



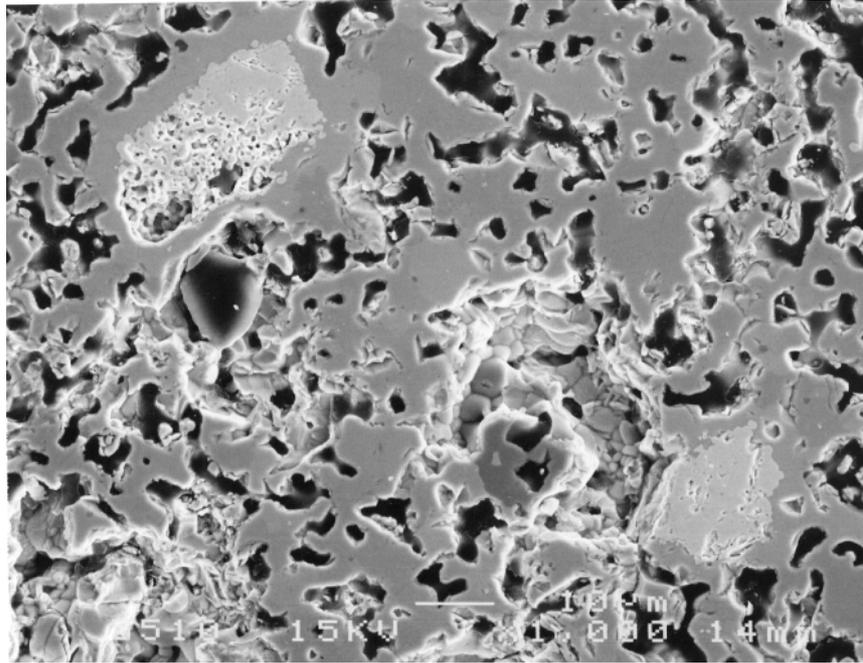
(a)



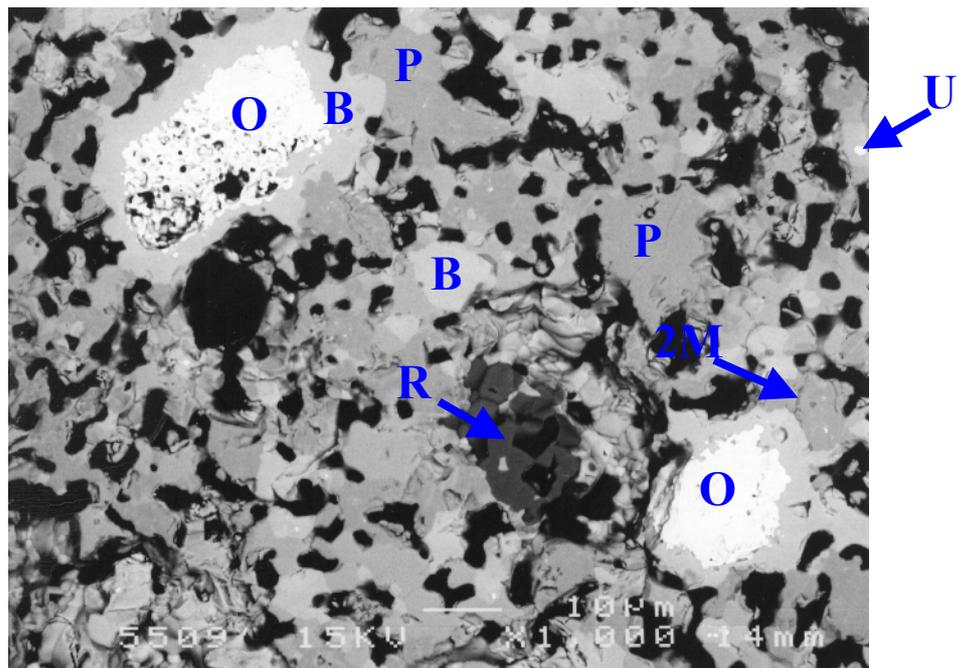
(b)

— 10 μm.

Figure E-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980175 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix), the light-grey phase is Th/U-brannerite and porosity (see (a)) is also present.



(a)



(b)

10 μm.

Figure E-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980147 (Task 1.2, composition B1-10, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The sample consists mainly of pyrochlore (P, mid-grey), 2M zirconolite (2M, darker grey) and Th/U-brannerite (B, light-grey). Unmilled ThO<sub>2</sub> (O, white regions surrounded by brannerite), UO<sub>2</sub> (U, small white spots) and Hf-doped rutile (R, dark-grey) are also present. The sample is porous (see (a)).

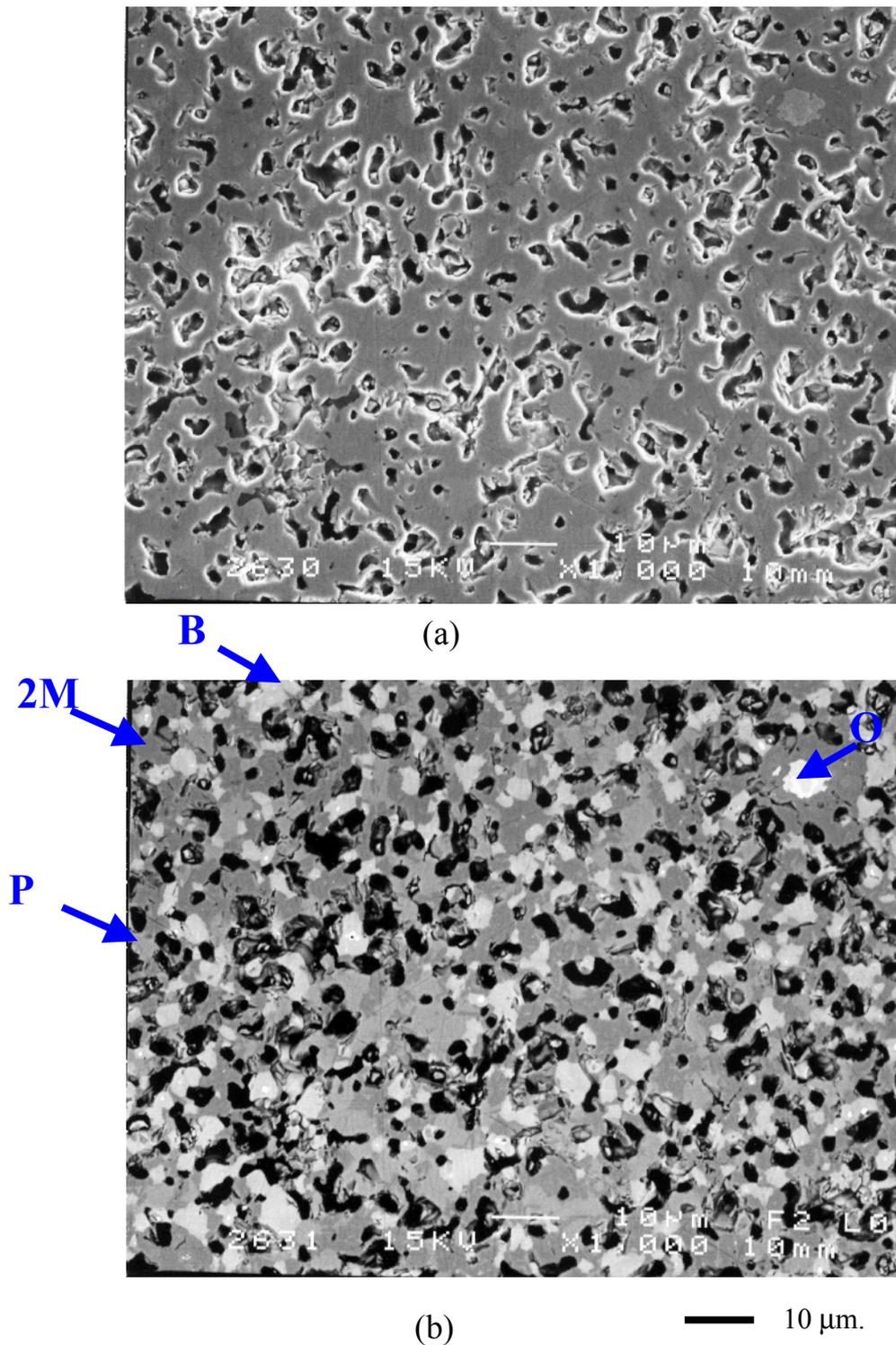
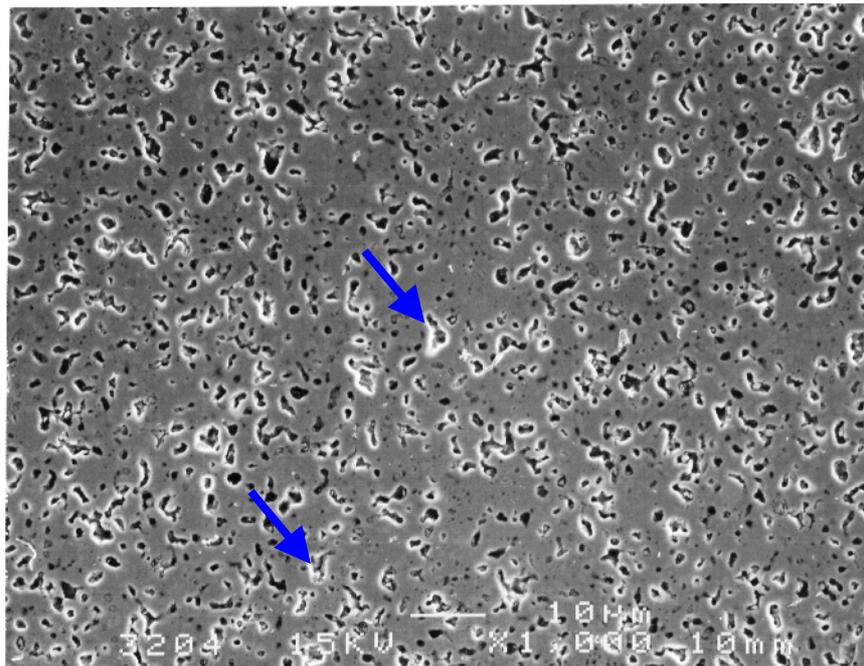
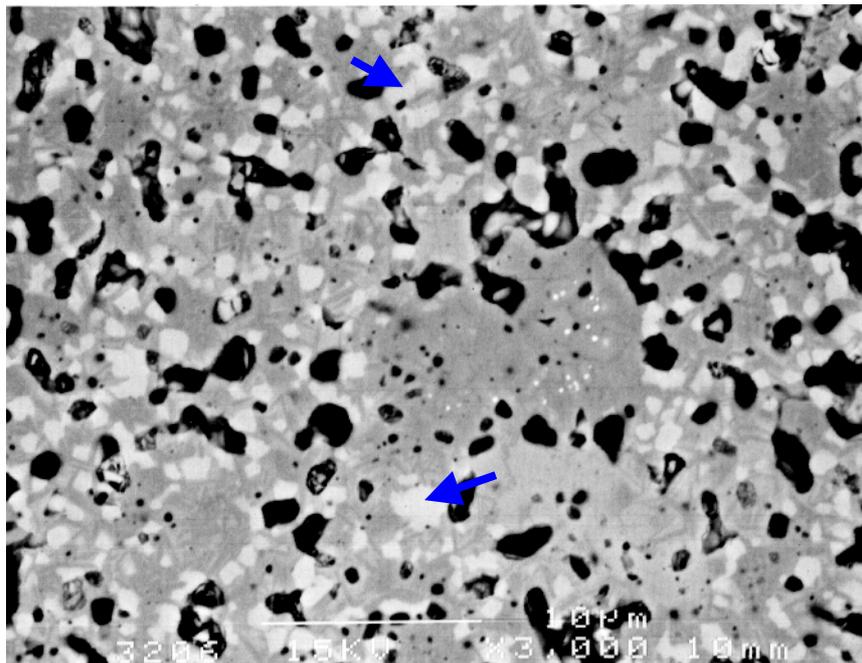


Figure E-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980145 (Task 1.2, composition B1-10, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The sample consists mainly of pyrochlore (mid-grey), 2M zirconolite (2M, darker grey) and Th/U-brannerite (B, light-grey). Some (< 1 vol. %) grains of ThO<sub>2</sub>-UO<sub>2</sub> (O) are also present inside the brannerite grains. The sample is porous (see (a)).



(a)

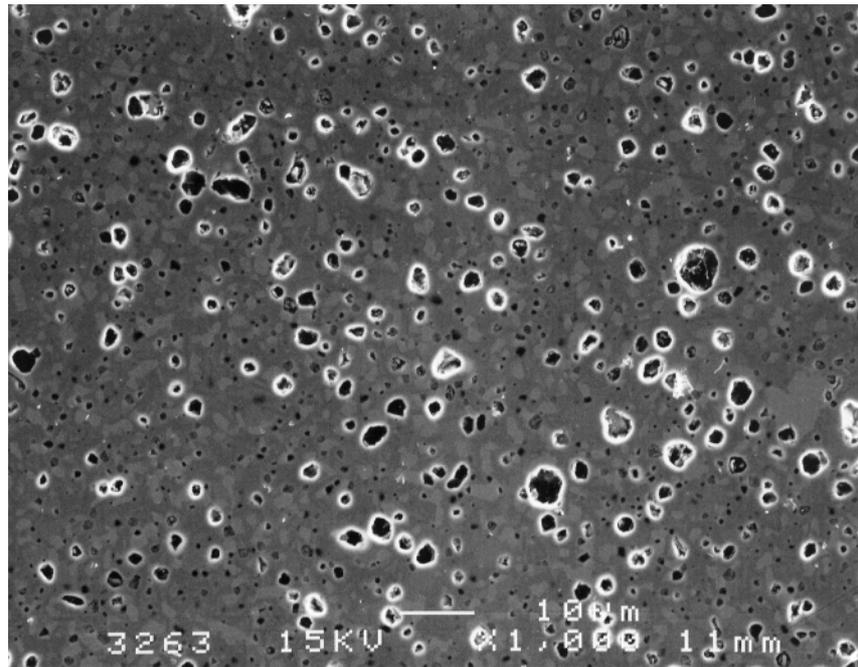
— 10  $\mu\text{m}$ .



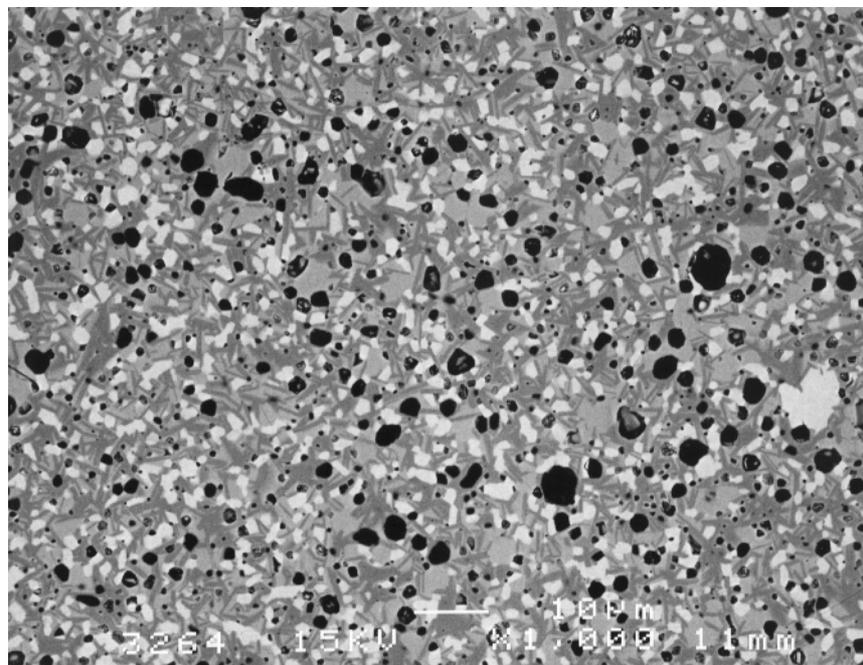
(b)

— 10  $\mu\text{m}$ .

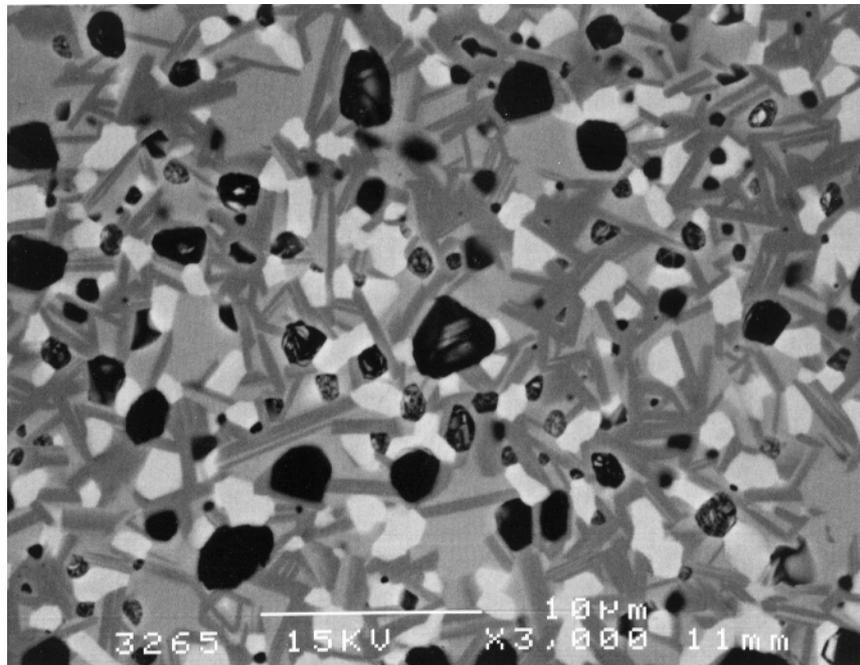
Figure E-5: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980311 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix), the light-grey phase is Th/U-brannerite (B) and porosity (A) is also present.



(a) — 10 µm.

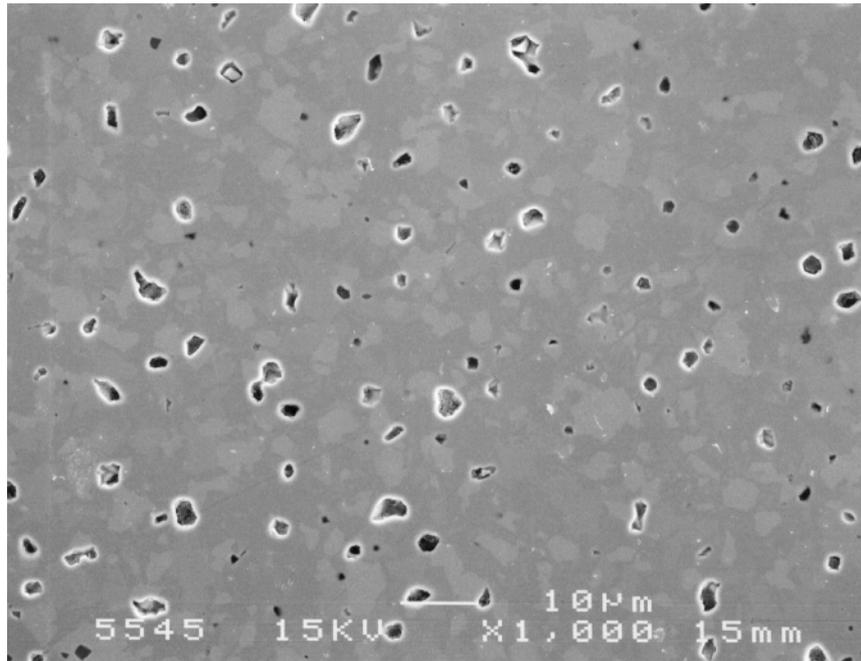


(b) — 10 µm.

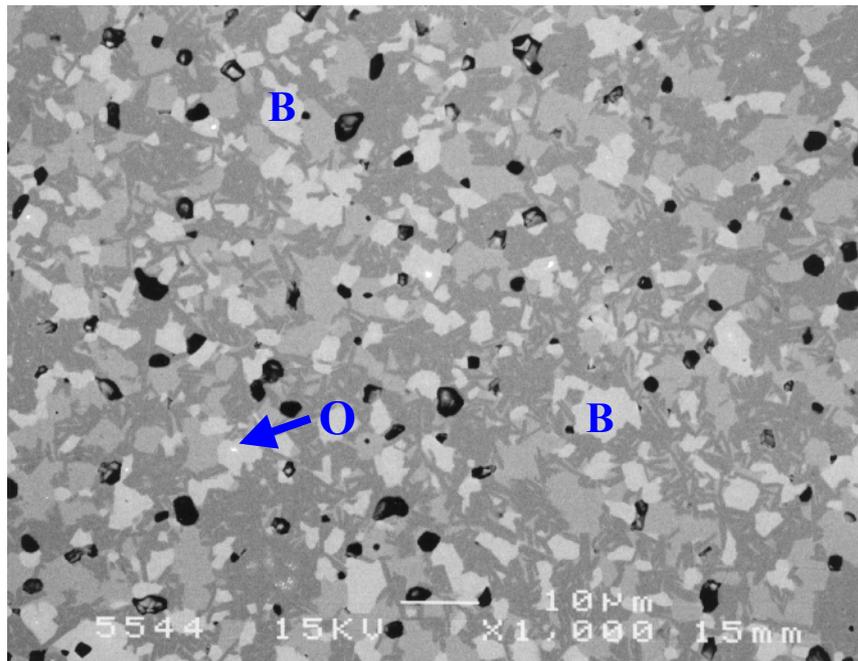


(c)  10 µm.

Figure E-6: (a) Secondary electron micrograph and, (b) and (c) backscattered electron micrographs of mws980325 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is pyrochlore, with 2M zirconolite (grey elongated grains) and brannerite (light-grey grains). Porosity is present (see (a)).



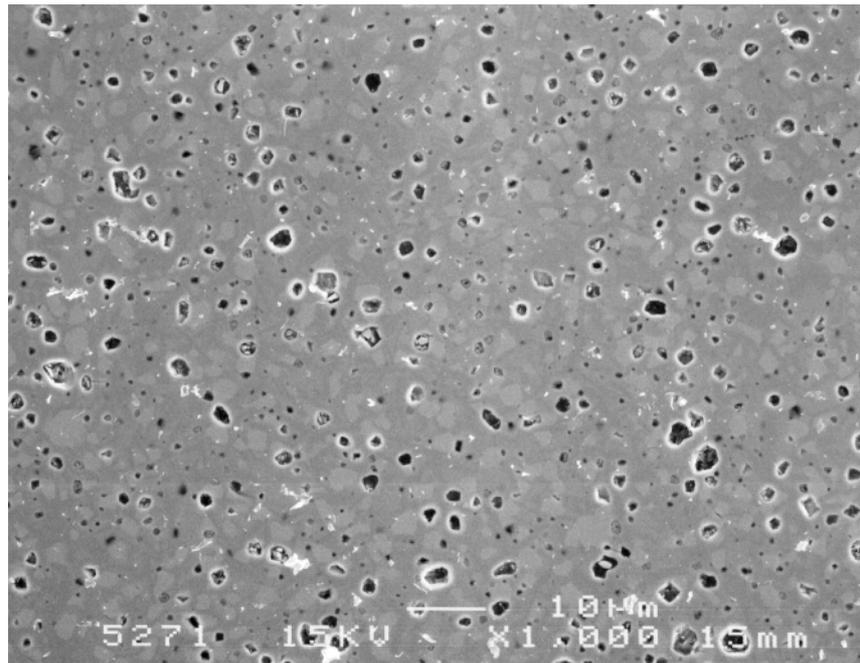
(a)



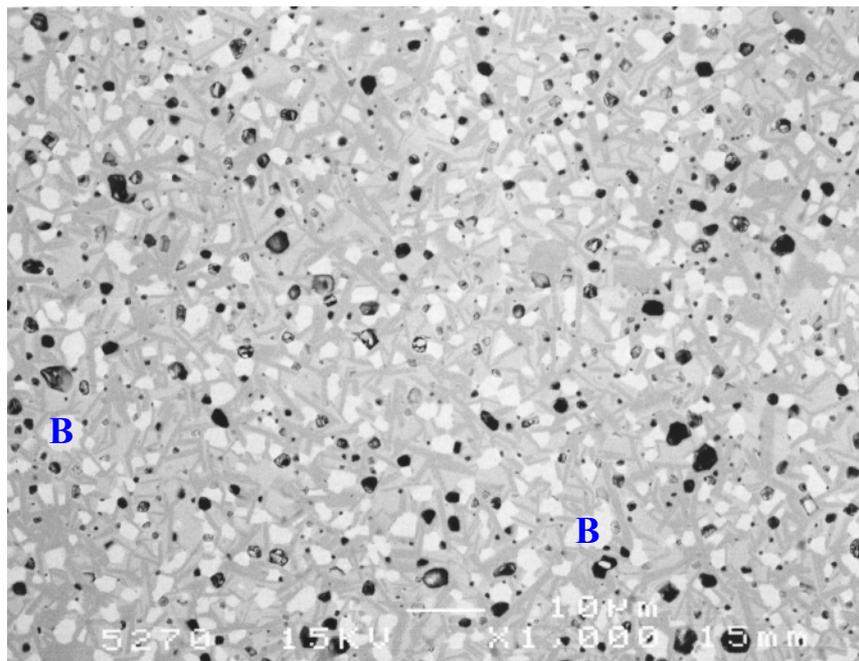
(b)

— 10 µm.

Figure E-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980409 (Task 1.2, composition B1-10, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix); the light-grey phase is Th/U-brannerite (B). A small amount of (Th,U)O<sub>2</sub> (O, white spots) and porosity (see (a)) is also present.



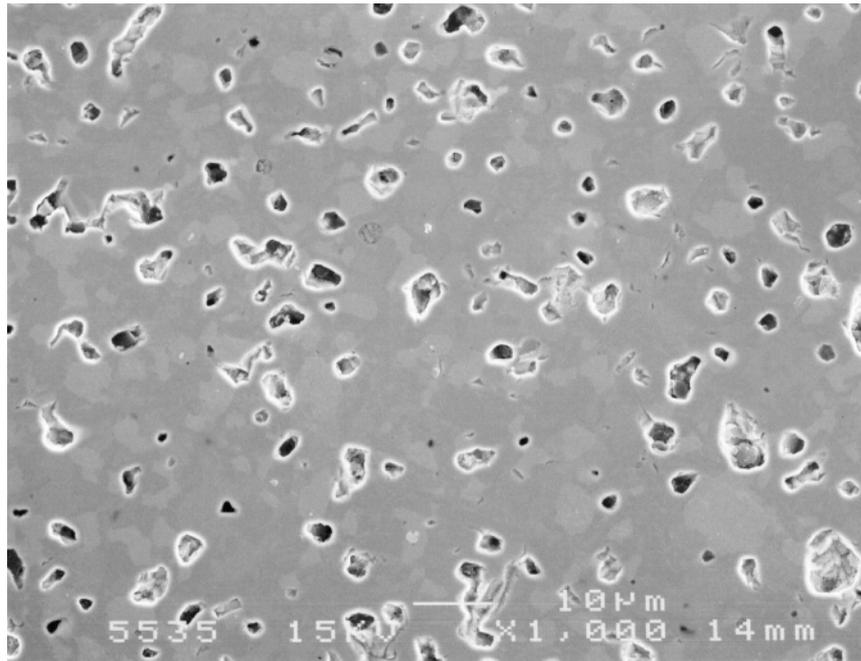
(a)



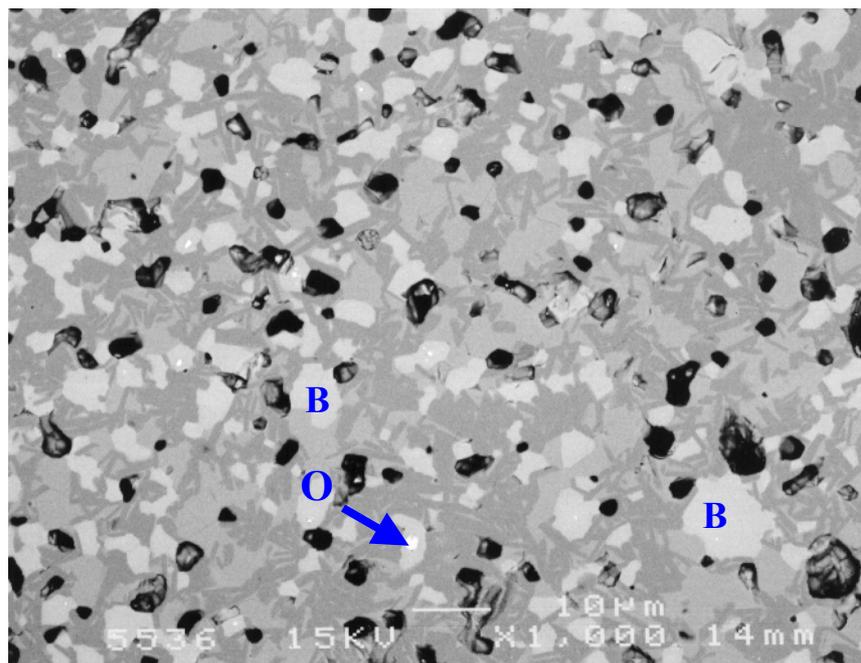
(b)

— 10 µm.

Figure E-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980349 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix), the light-grey phase is Th/U-brannerite (B) and porosity (see (a)) is also present.



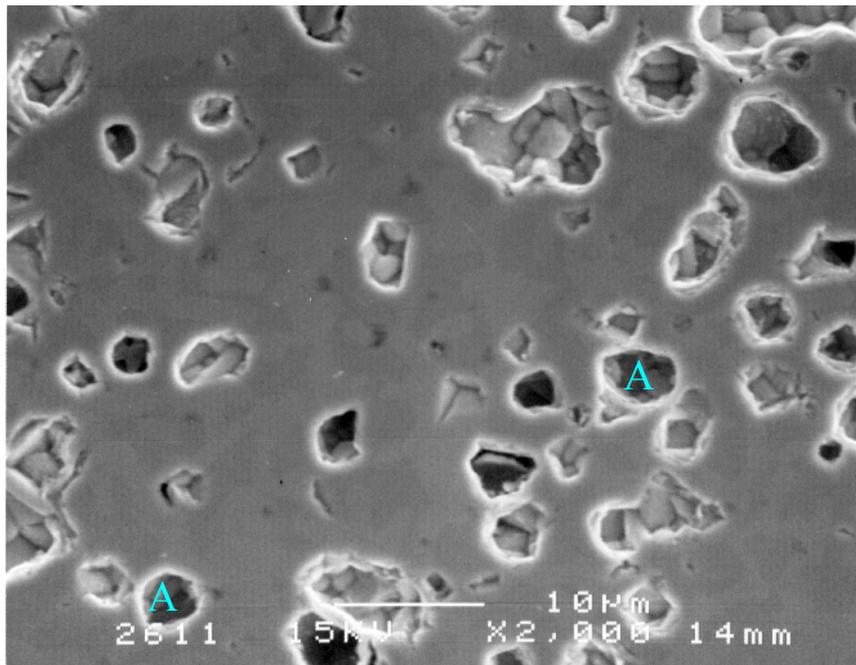
(a)



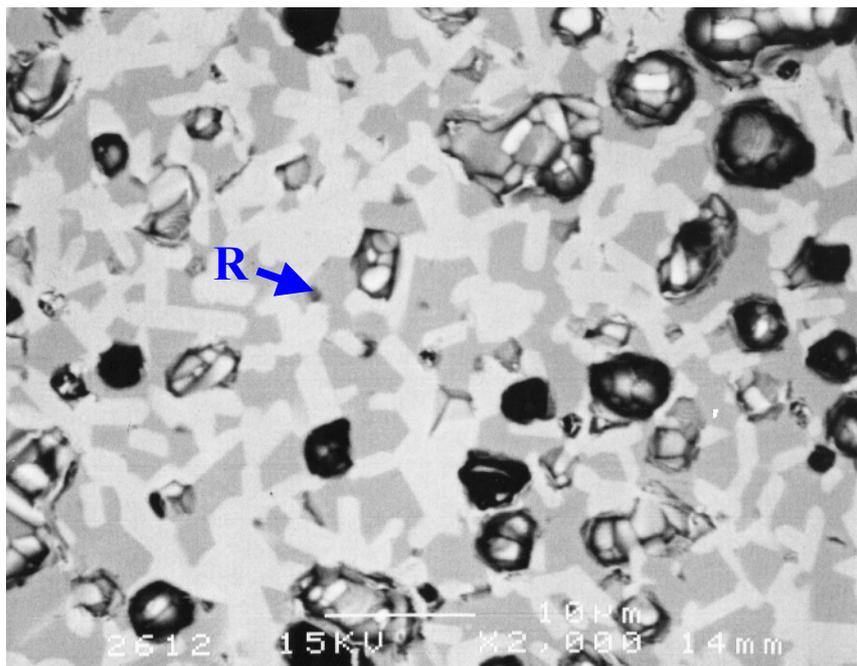
(b)

— 10 μm.

Figure E-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980395 (Task 1.2, composition B1-10, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The matrix is a mixture of pyrochlore (mid-grey) and 2M zirconolite (darker grey in matrix), the light-grey phase is Th/U-brannerite (B); some (Th,U)O<sub>2</sub>O, white spots in brannerite) and porosity (see (a)) are present.

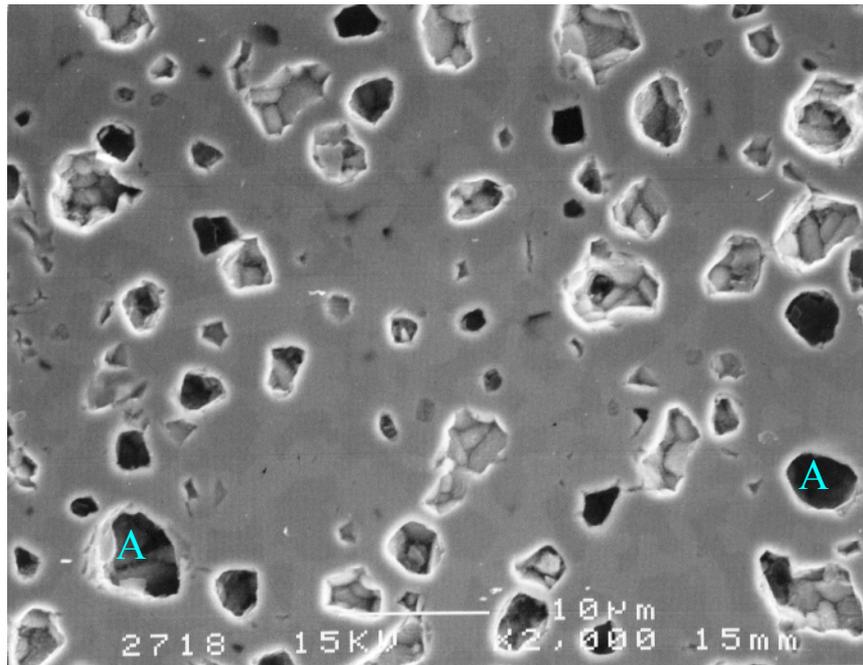


(a)

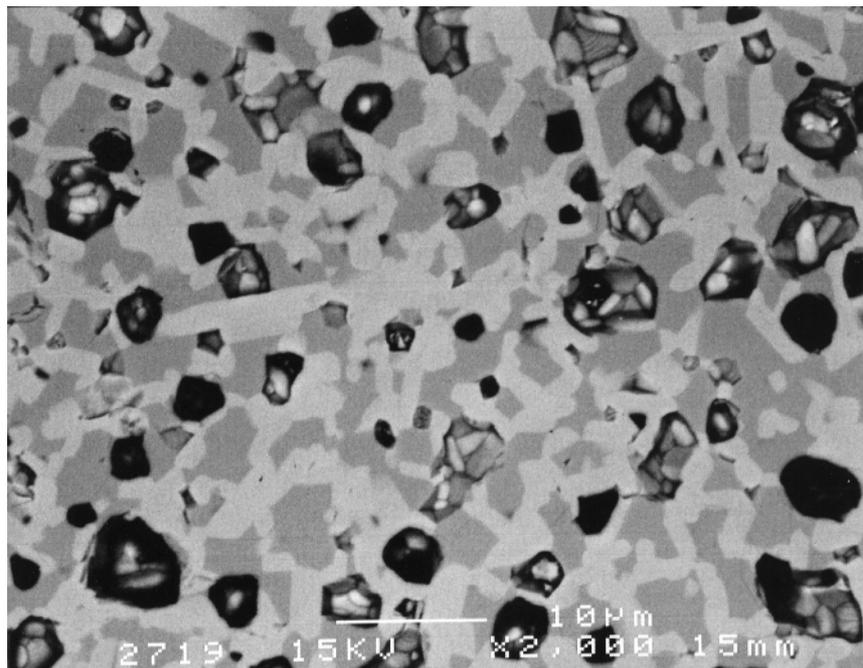


(b)  10 μm.

Figure F-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980110 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 4 hours, sintered at 1350°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase); some Hf-doped rutile (R, dark-grey phase) is also present, as is porosity (A).

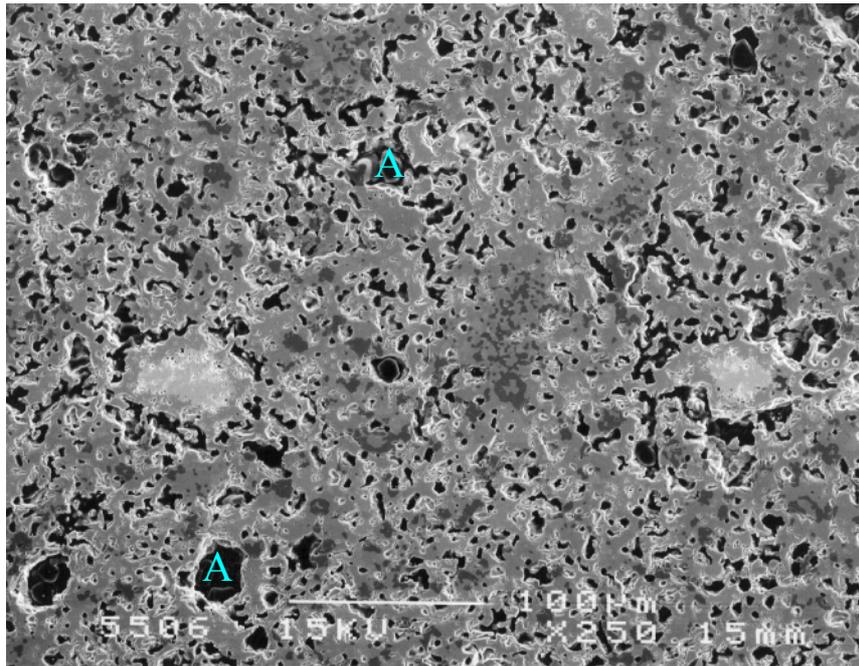


(a)

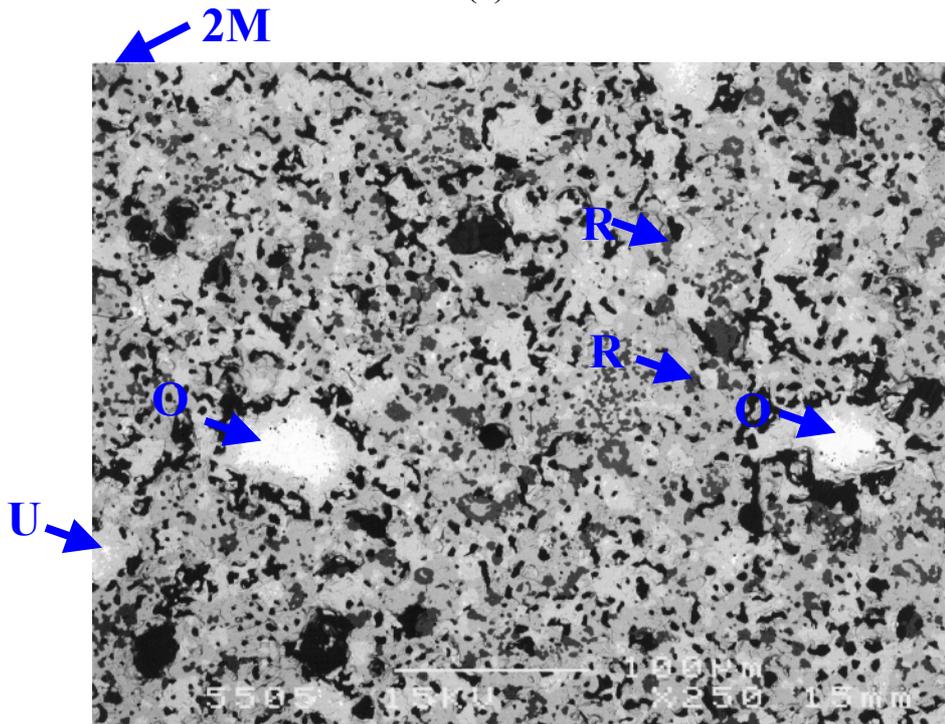


(b)  10  $\mu\text{m}$ .

Figure F-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980179 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours. The sample is a mixture of pyrochlore (mid-grey phase), Th/U-brannerite (light-grey phase) and some porosity (A).

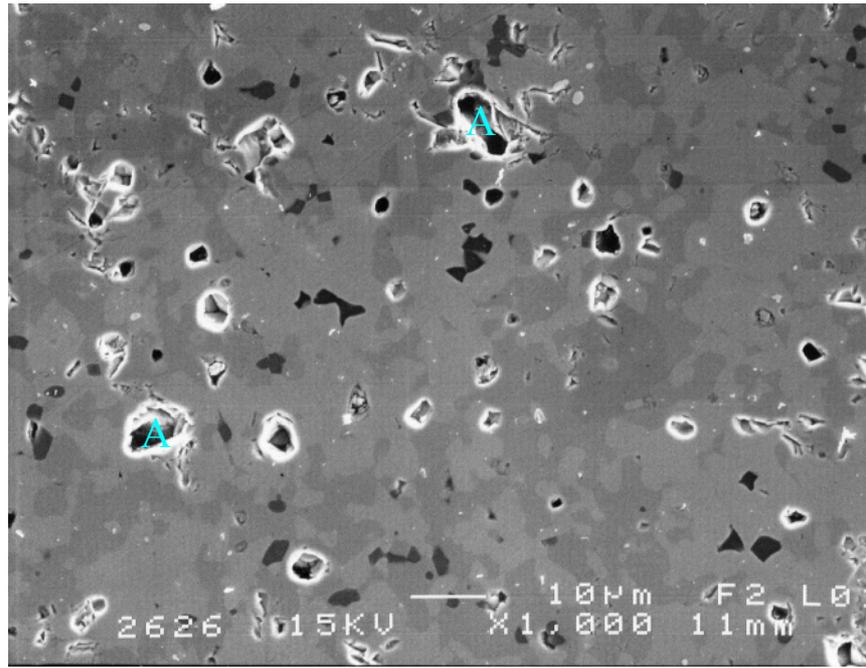


(a)

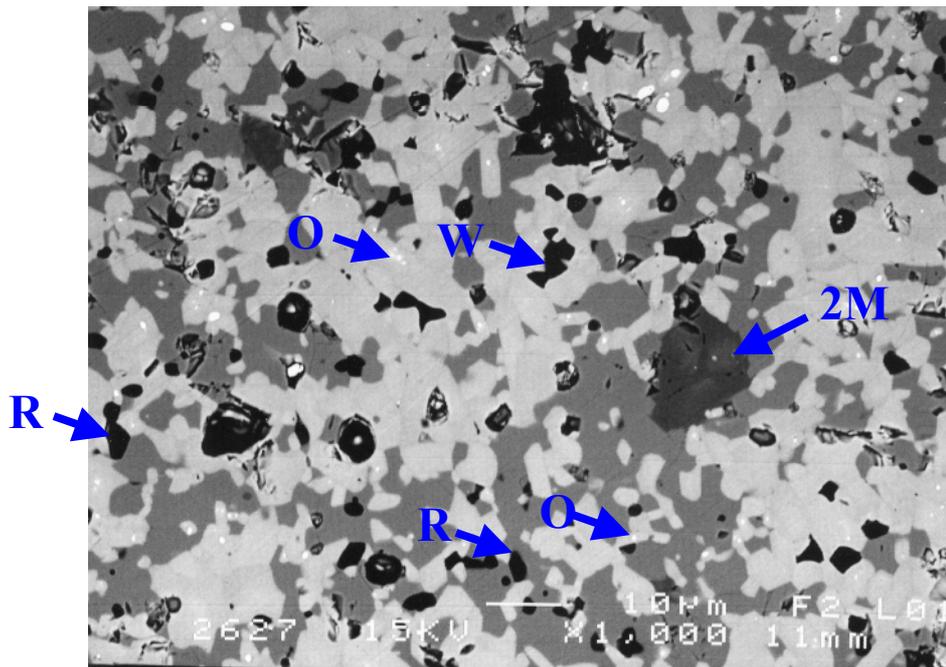


(b)  100  $\mu\text{m}$ .

Figure F-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980143 (Task 1.2, composition B1-12, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase). Also present are 2M zirconolite (2M), Hf-doped rutile (R, dark-grey), ThO<sub>2</sub> (O, white) and porosity (A). < 1 vol. % of UO<sub>2</sub> (U, fine white grains – same contrast as ThO<sub>2</sub>), and whitlockite were also detected in the sample.



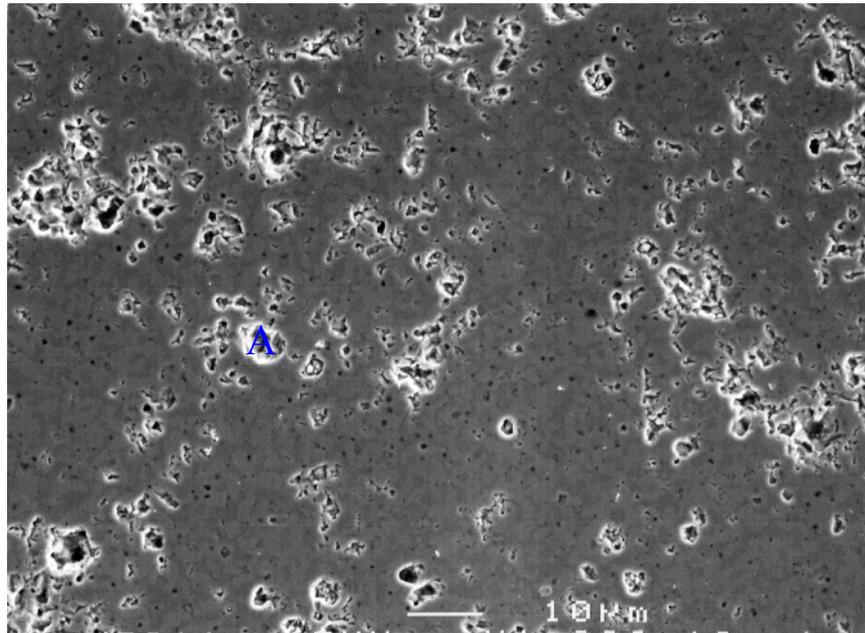
(a)



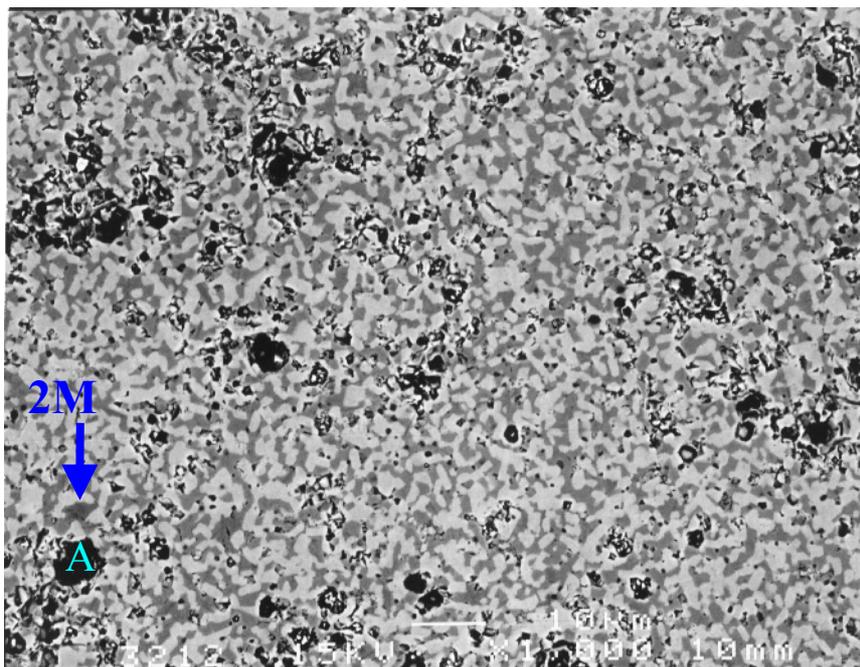
(b)

— 10 µm.

Figure F-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980141 (Task 1.2, composition B1-12, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours. The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase). Also present are 2M zirconolite (2M), Hf-doped rutile (R, dark-grey),  $\text{ThO}_2\text{-UO}_2$  (O, white), whitlockite (W) and porosity (A).



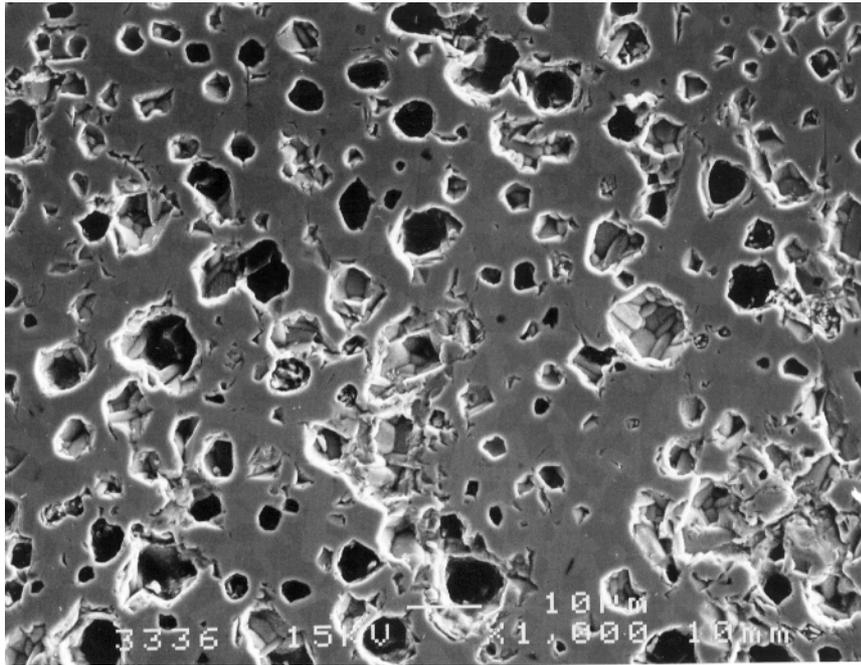
(a)



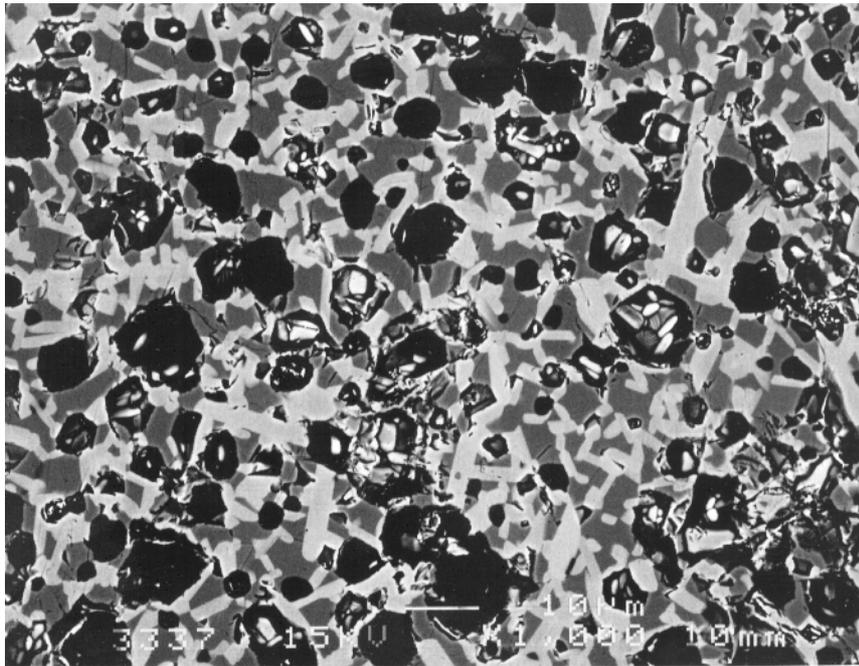
(b)

— 10 μm.

Figure F-5: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980313 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours. The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase). 2M zirconolite (2M, dark-grey phase) is also present, as is porosity (A).



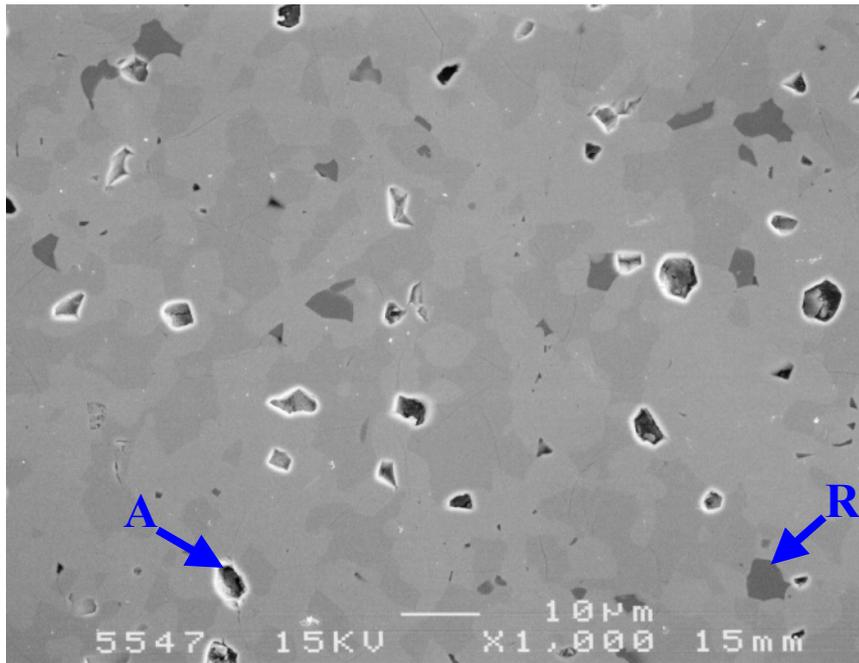
(a)



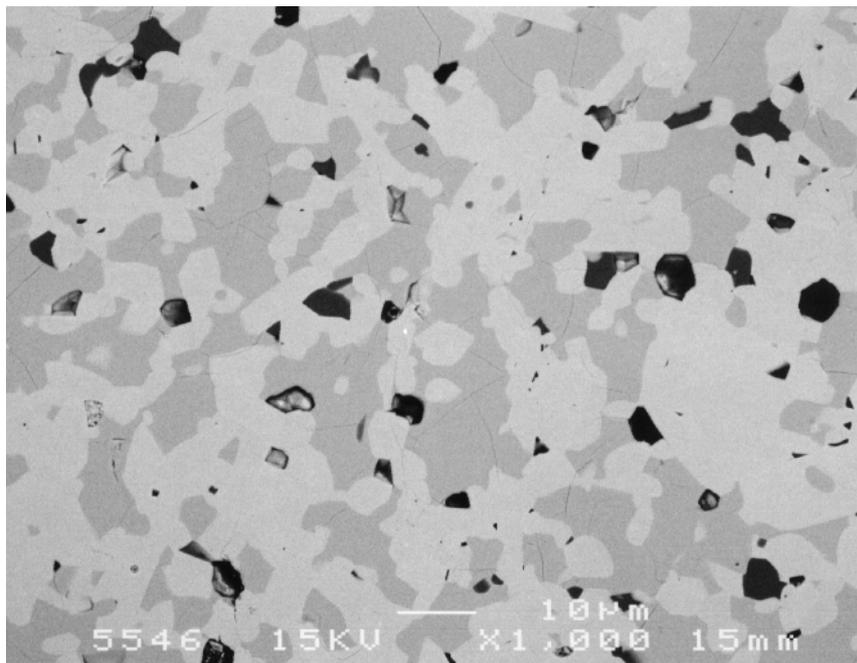
(b)

— 10 μm.

Figure F-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980326 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The sample consists of a mixture of pyrochlore (grey), and brannerite (light grey). Porosity (see (a)) is present.

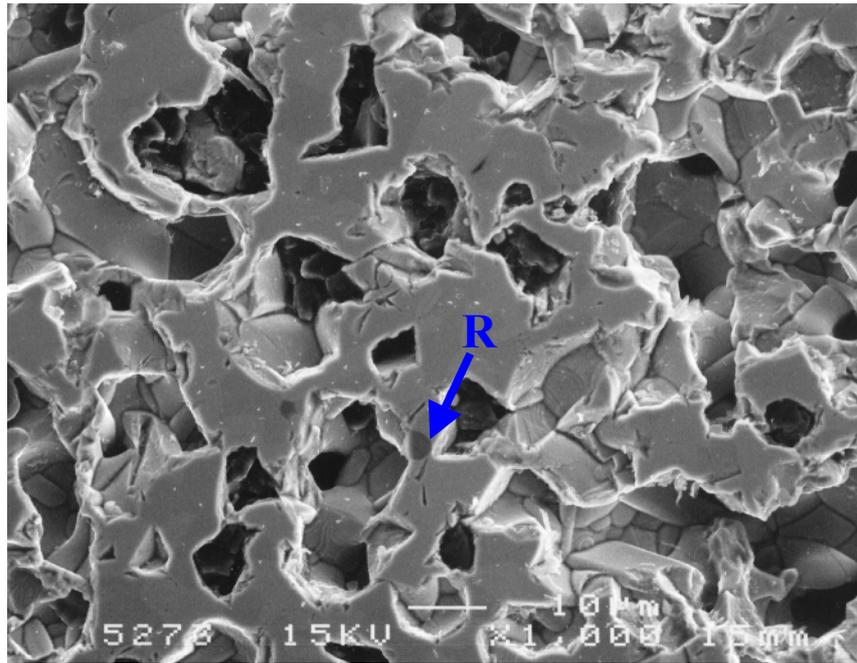


(a)

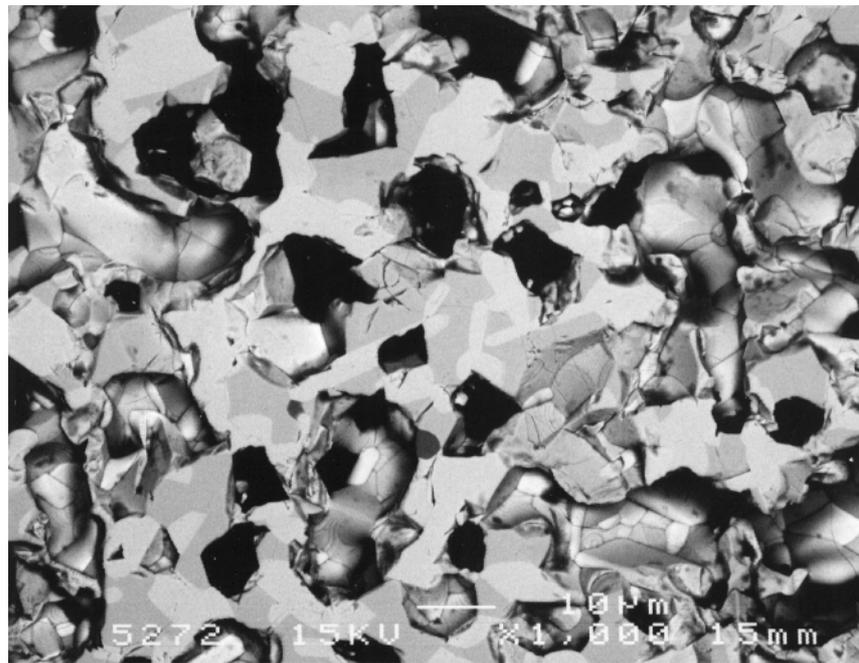


(b) — 10 µm.

Figure F-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980410 (Task 1.2, composition B1-12, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The sample consists of a mixture of pyrochlore (grey) and brannerite (light grey), with some Hf-doped rutile (dark-grey grains, R). Porosity (A) is also present.

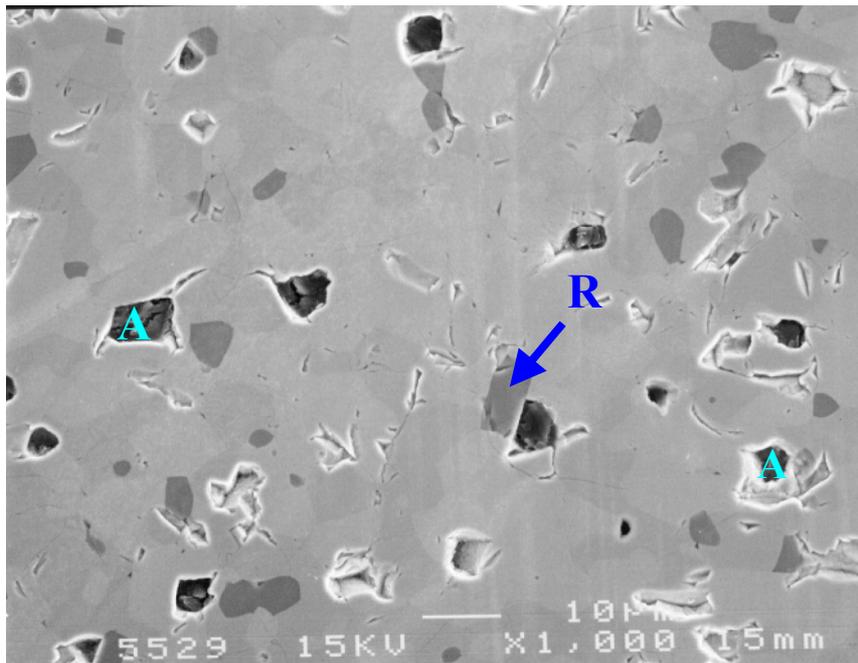


(a)

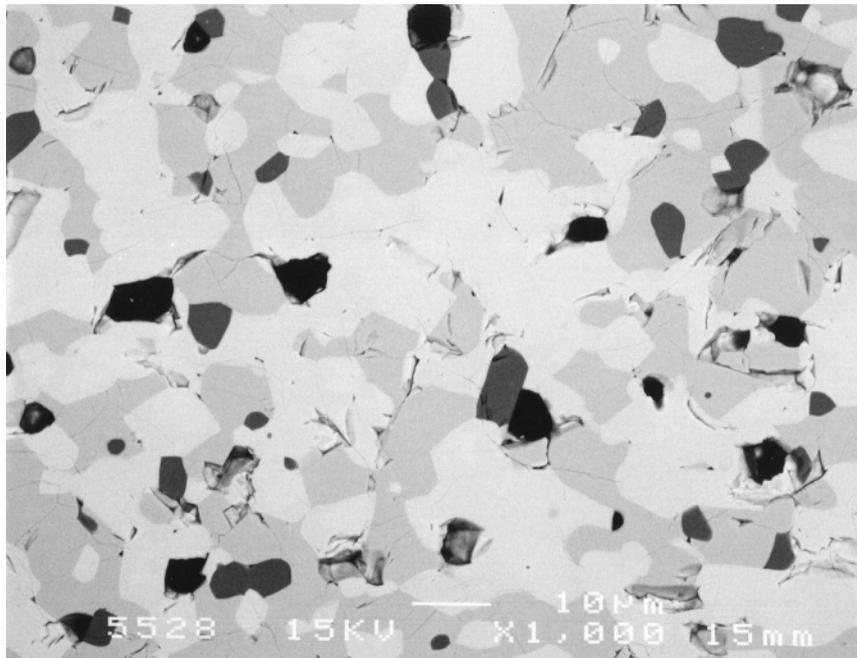


(b) — 10 µm.

Figure F-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980350 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The sample consists of a mixture of pyrochlore (grey) and brannerite (light grey), with some Hf-doped rutile (dark-grey grains, R). The sample is very porous (see (a)).

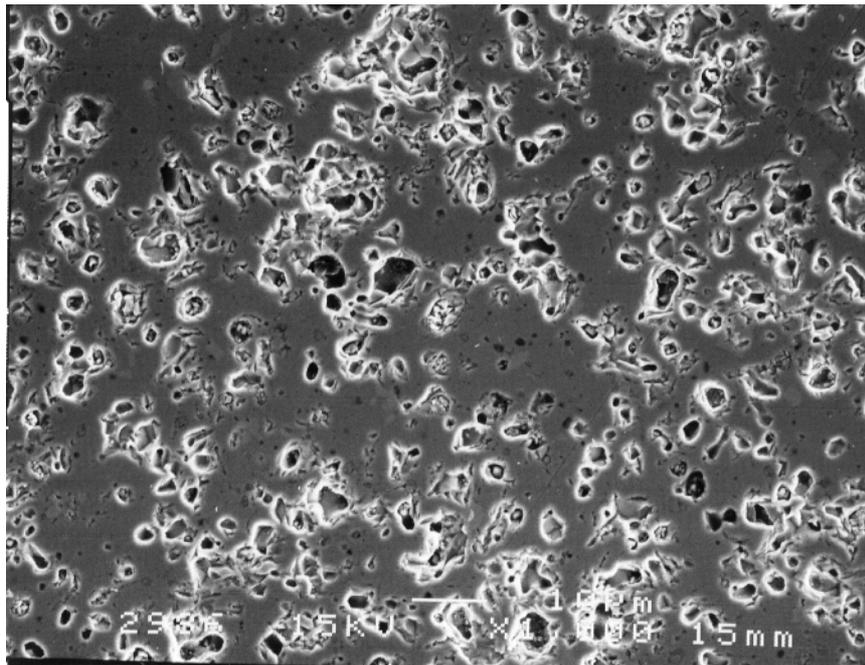


(a)

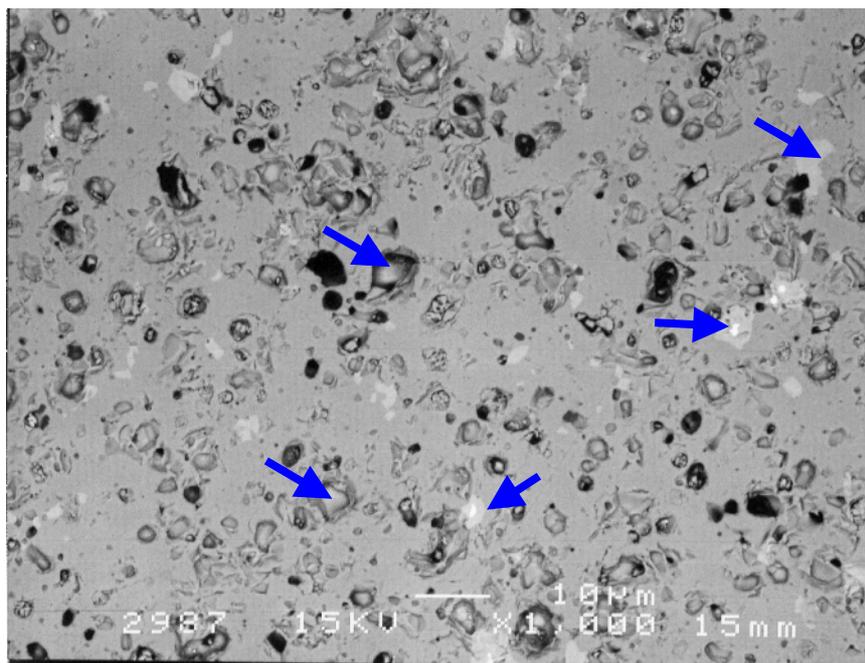


(b) — 10 µm.

Figure F-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980396 (Task 1.2, composition B1-12, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The sample consists of a mixture of pyrochlore (grey) and brannerite (light grey), with some Hf-doped rutile (dark-grey grains, R) and porosity (A) present.



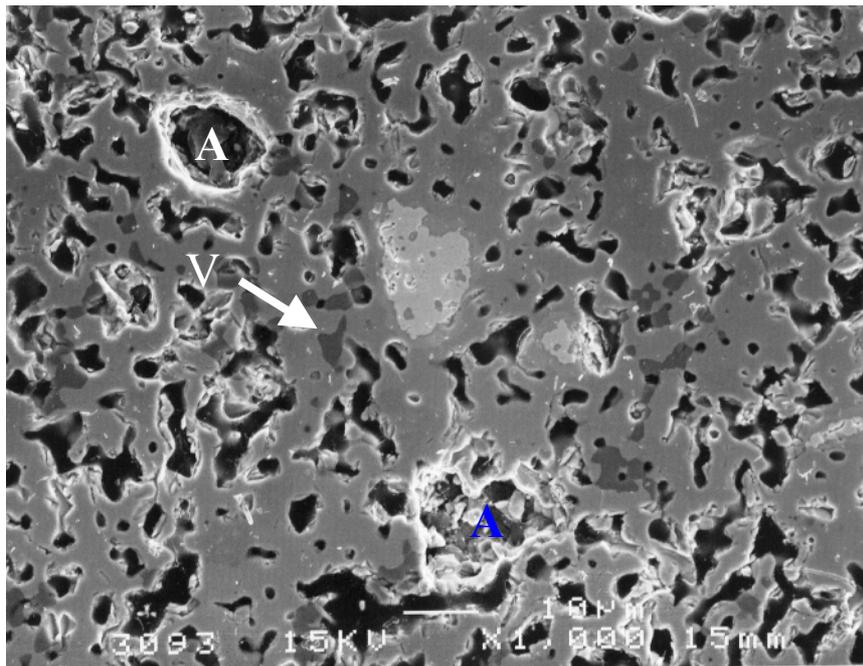
(a)



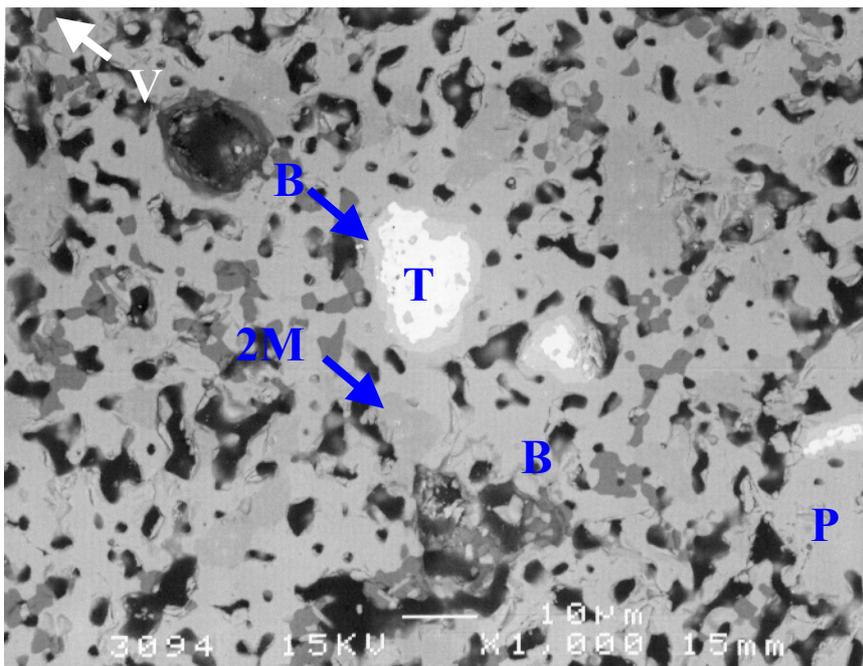
(b)

— 10  $\mu\text{m}$ .

Figure G-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980262 (Task 1.2, composition B1-14, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore, the light-grey phase is Th/U-brannerite (B) and the white regions inside the grains are ThO<sub>2</sub> (O). Porosity (A) is present.



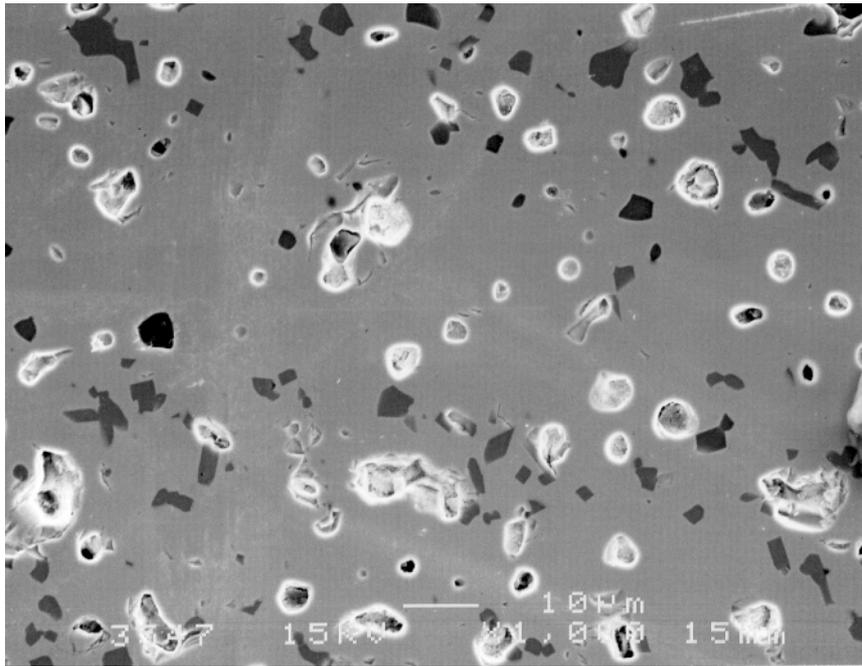
(a)



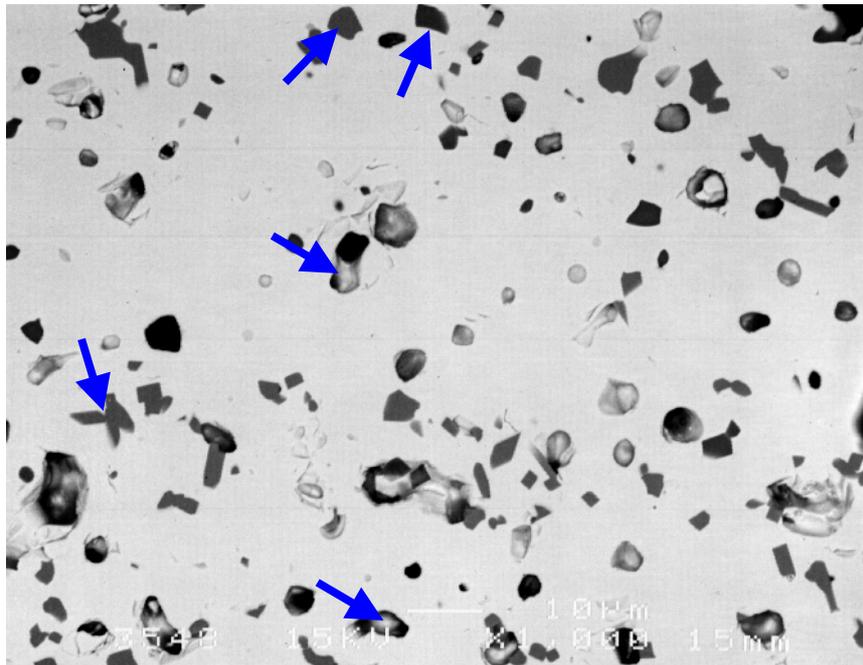
(b)

— 10  $\mu\text{m}$ .

Figure G-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980283 (Task 1.2, composition B1-14, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P) with Th/U-brannerite (B) grains of variable composition, some of which have ThO<sub>2</sub> cores. There is also 2M zirconolite (2M, in (b) this phase is slightly darker grey than the matrix pyrochlore), porosity (A) and perovskite present (V, dark-grey).

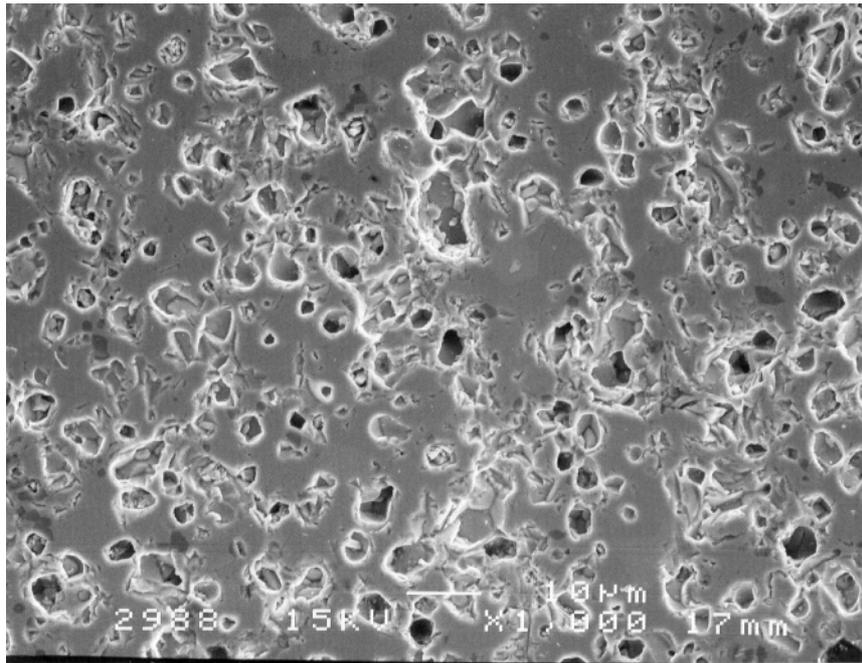


(a)

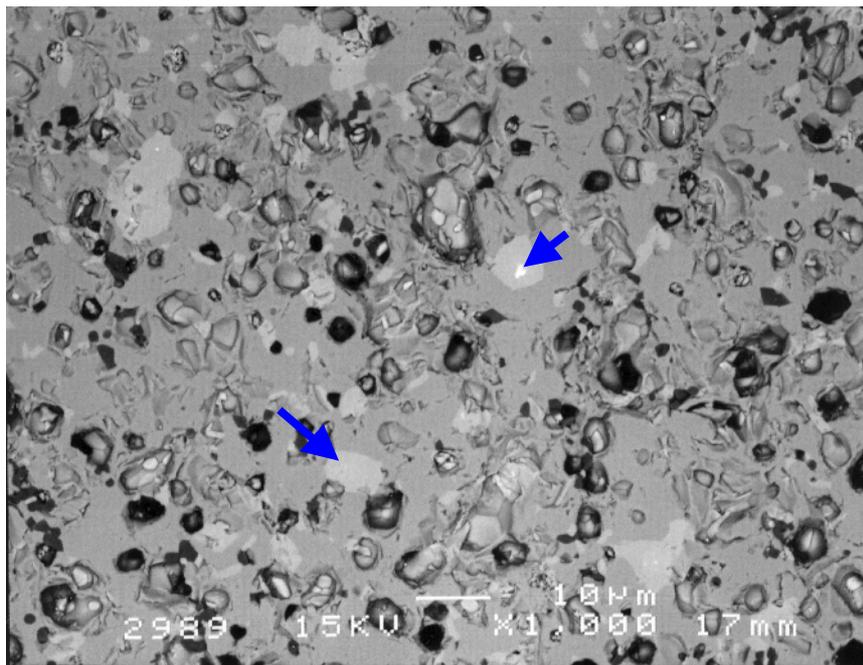


(b) — 10 μm.

Figure G-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980258 (Task 1.2, composition B1-14, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore, with some Hf-doped rutile (R) and porosity (A). Some whitlockite (W, dark-grey-black grains) is also present. Brannerite was not detected.



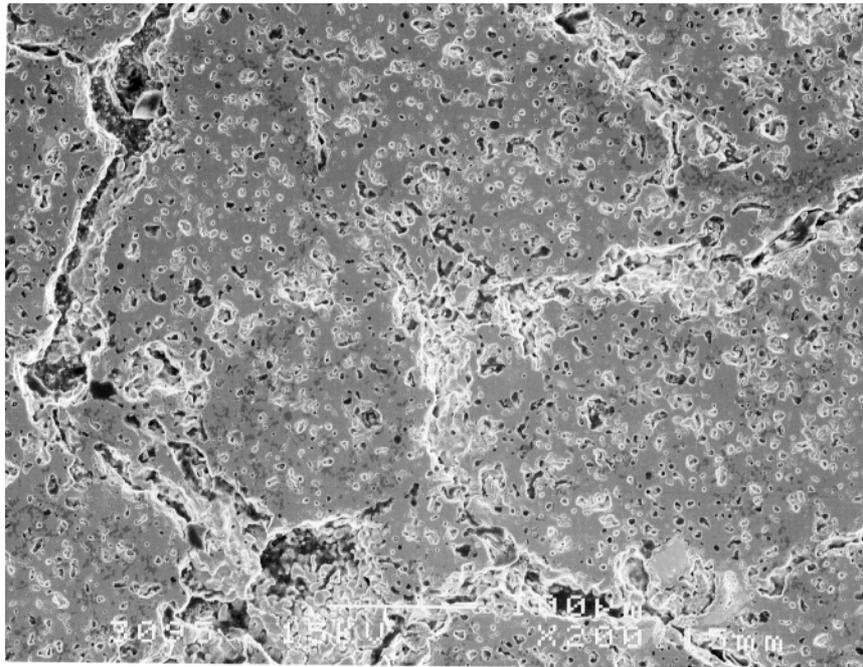
(a)



(b)

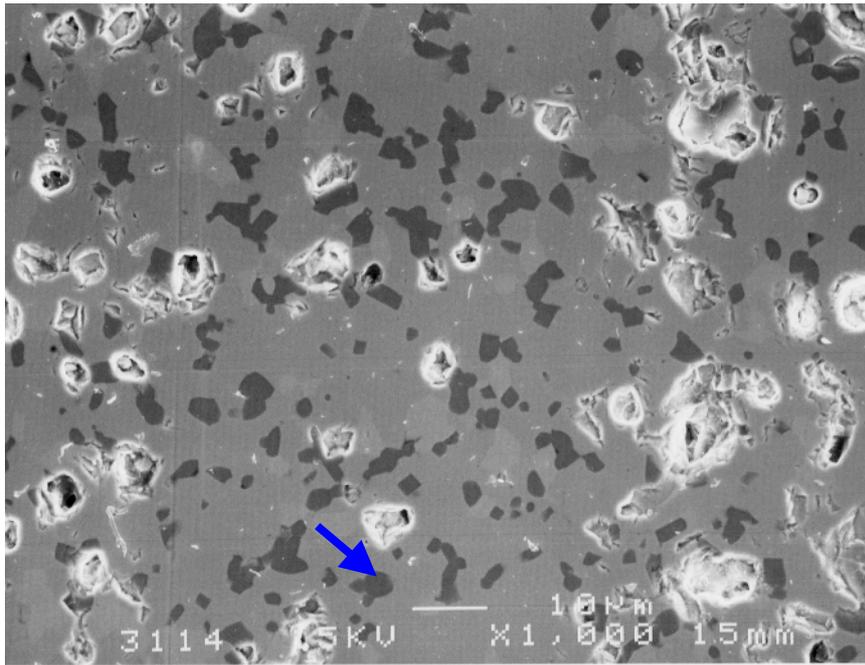
— 10 µm.

Figure G-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980268 (Task 1.2, composition B1-14, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The pellet is very porous and consists of a matrix of pyrochlore (P) with Th/U-brannerite (B) grains, some of which have a small amount of ThO<sub>2</sub> (T) inside.

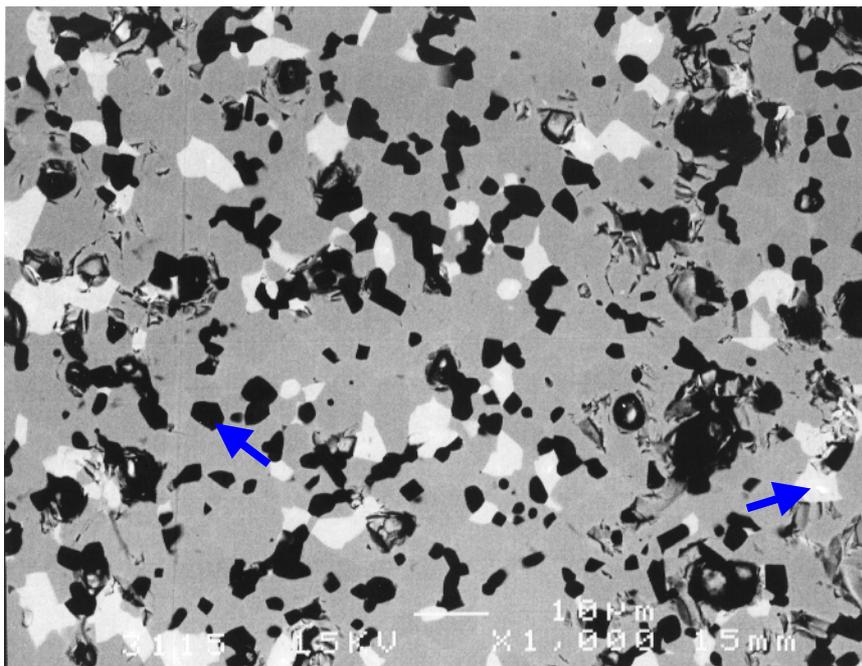


— 100  $\mu\text{m}$ .

Figure G-5: Secondary electron micrograph mws980288 (Task 1.2, composition B1-14, oxide-route, dry-milled 16 hours, sintered at 1350°C in air for 4 hours). The pellet is very inhomogeneous and porous. The composition varies across the pellet. It is composed mainly of pyrochlore, with some 2M zirconolite, Th/U-brannerite and thoria.



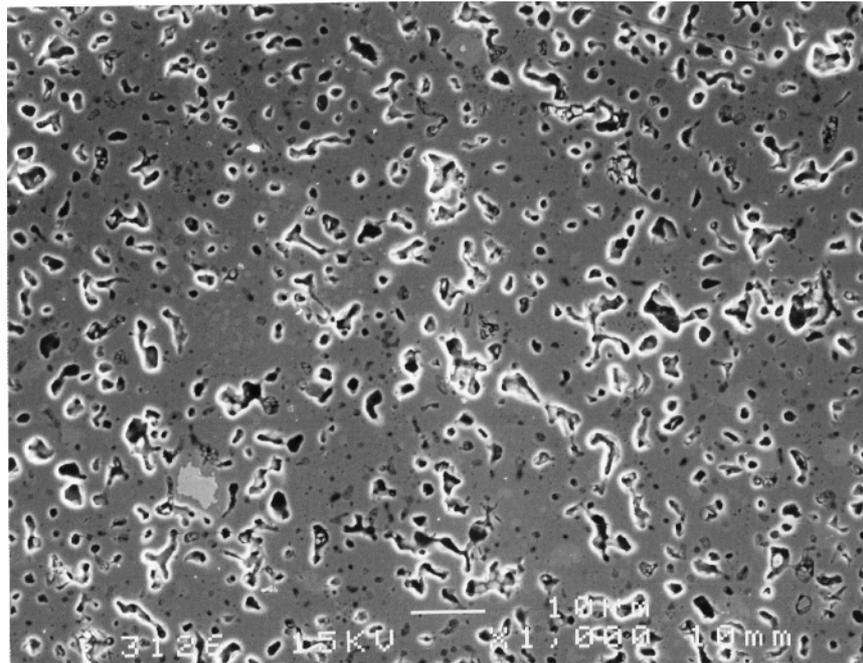
(a)



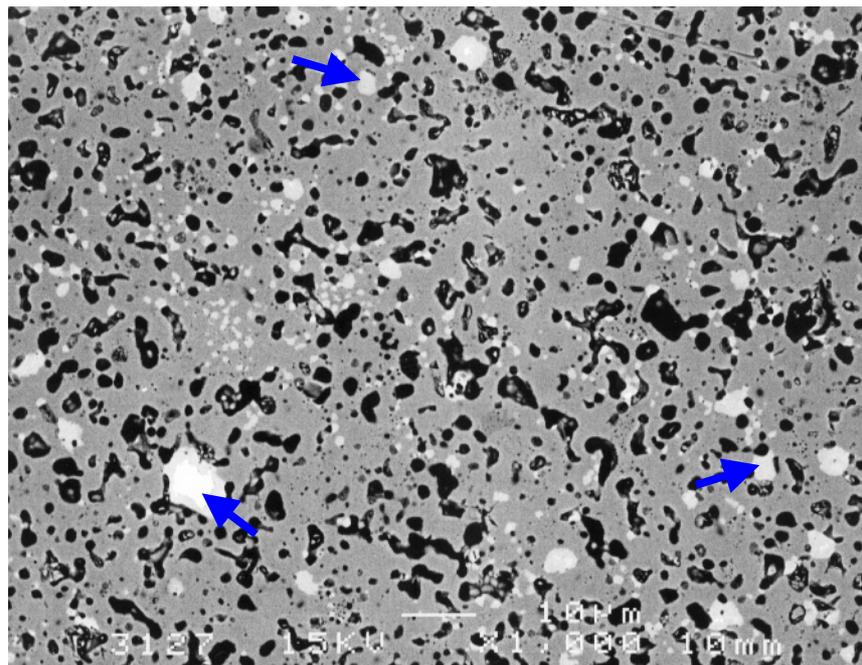
(b)

— 10  $\mu$ m.

Figure G-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980286 (Task 1.2, composition B1-14, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The pellet consists of a matrix of pyrochlore (P) with Th/U-brannerite (B) grains, Hf-doped rutile (R, dark-grey), porosity (A) and < 1 vol. % ThO<sub>2</sub> (T) located inside the Th/U-brannerite grains.



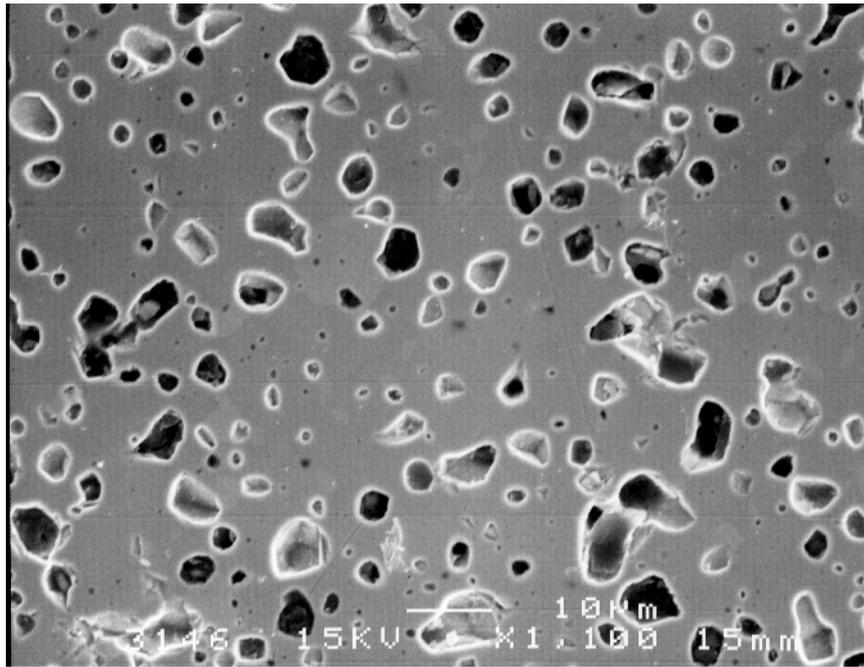
(a)



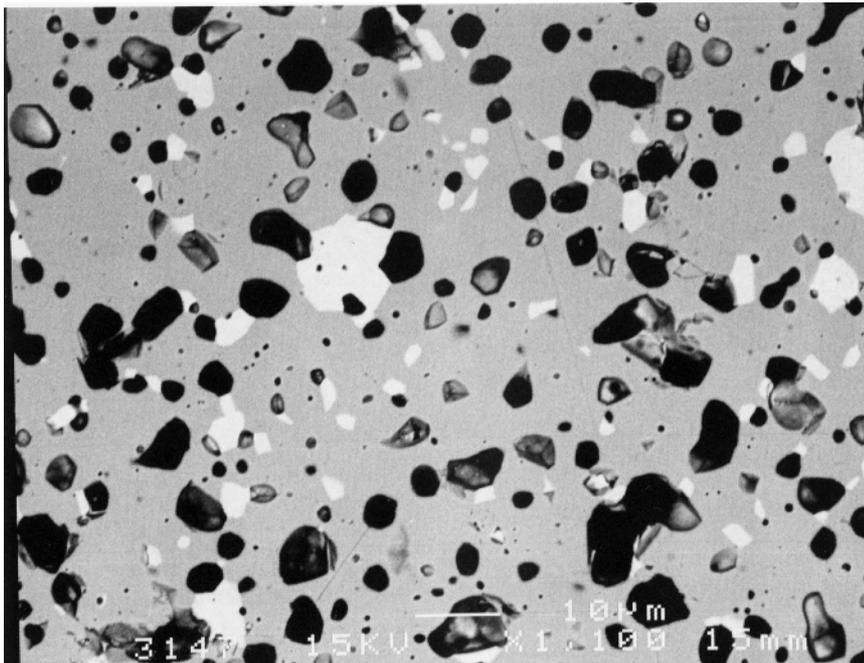
(b)

— 10 μm.

Figure G-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980319 (Task 1.2, composition B1-14, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The pellet is porous (see (a)) and consists of a matrix of pyrochlore (P), with Th/U-brannerite (B) grains and 2-3 vol. % ThO<sub>2</sub> (T) located in the Th/U-brannerite grains.



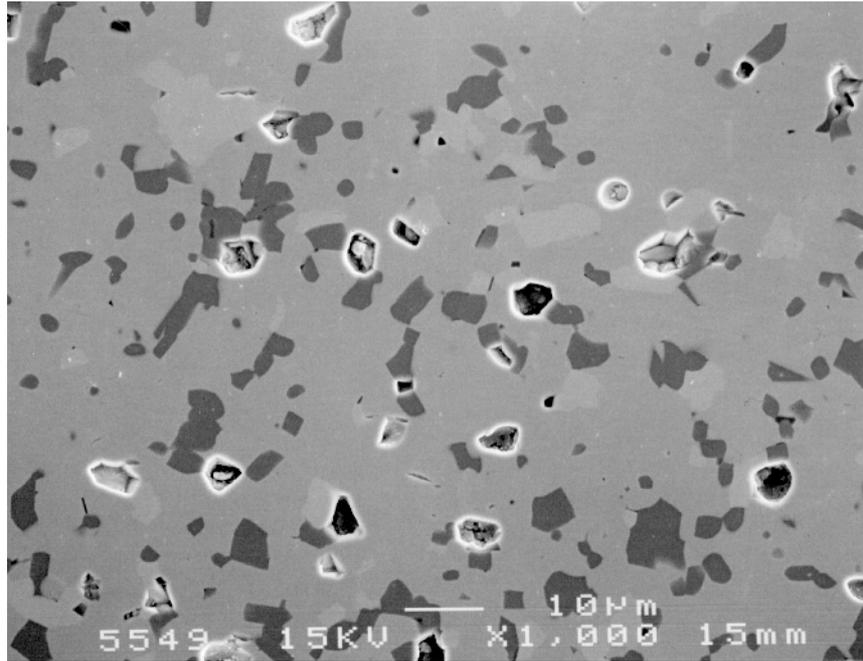
(a)



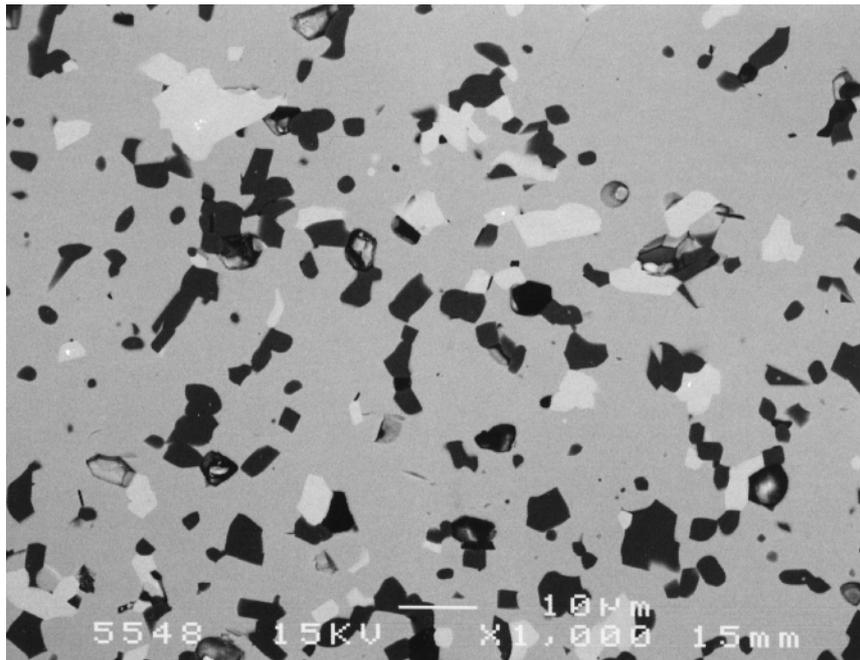
(b)

— 10 µm.

Figure G-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980305 (Task 1.2, composition B1-14, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P), with Th/U-brannerite grains (B, light-grey) and a significant amount of porosity (A).



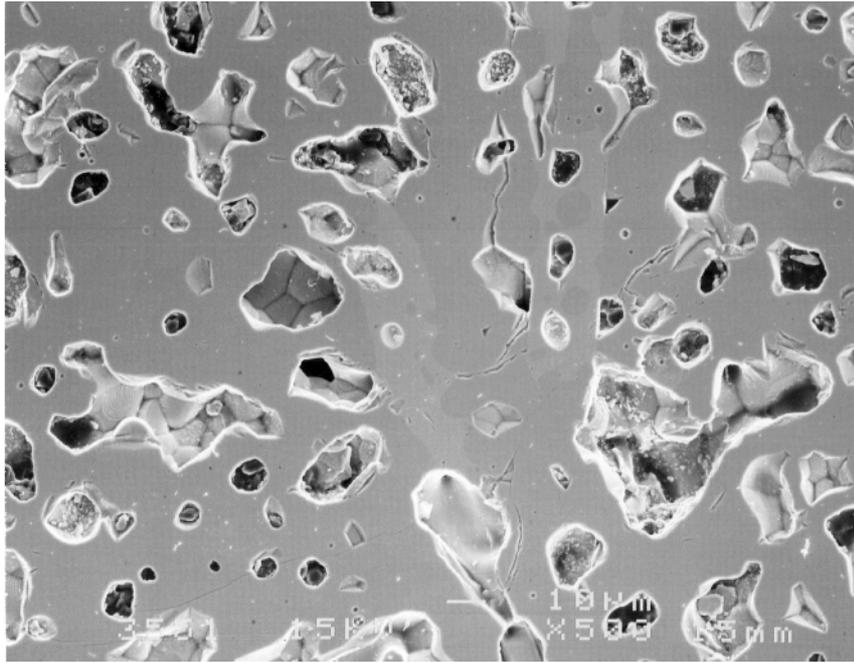
(a)



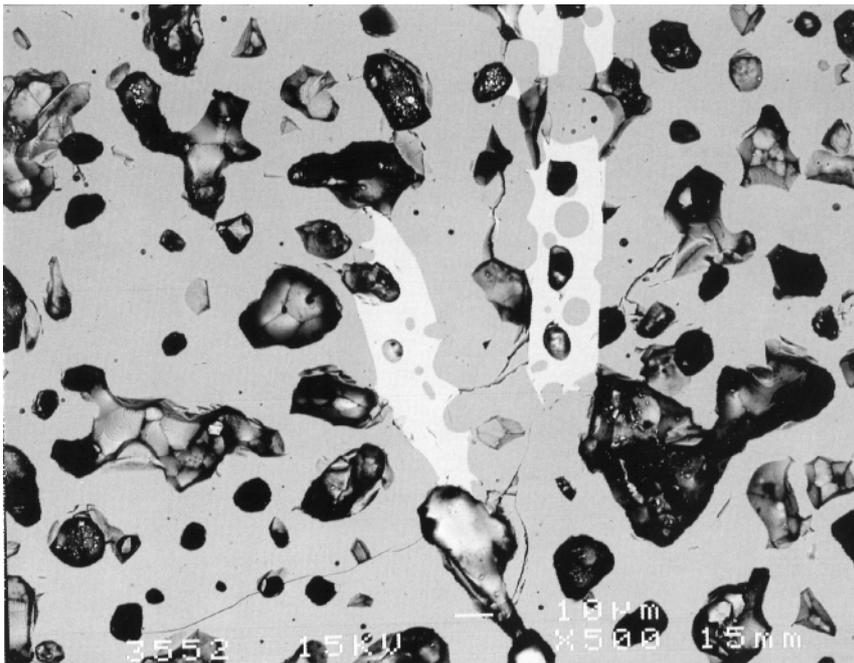
(b)

— 10 µm.

Figure G-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980411 (Task 1.2, composition B1-14, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P) with Th/U-brannerite grains (B, light-grey), Hf-doped rutile (R, dark-grey) and porosity (A).



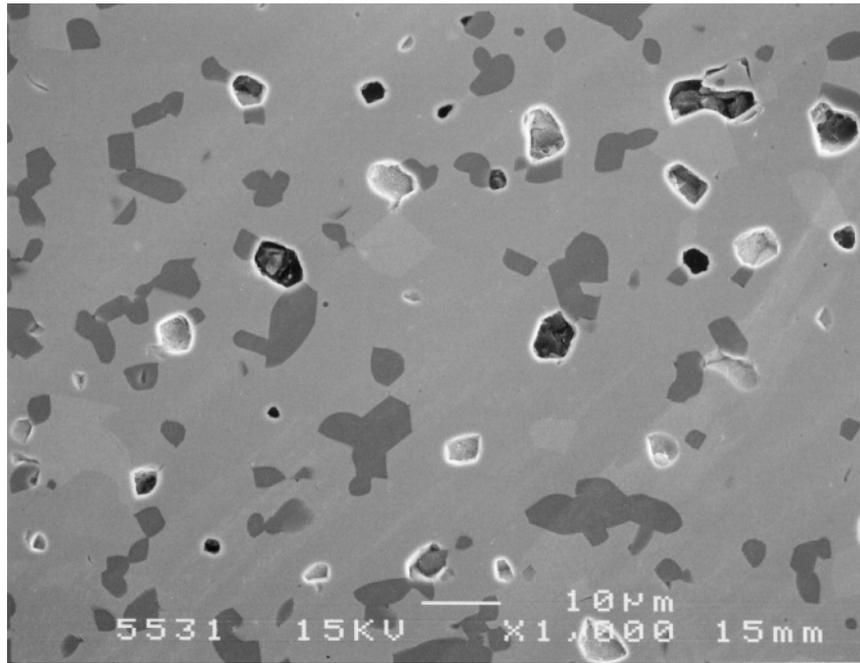
(a)



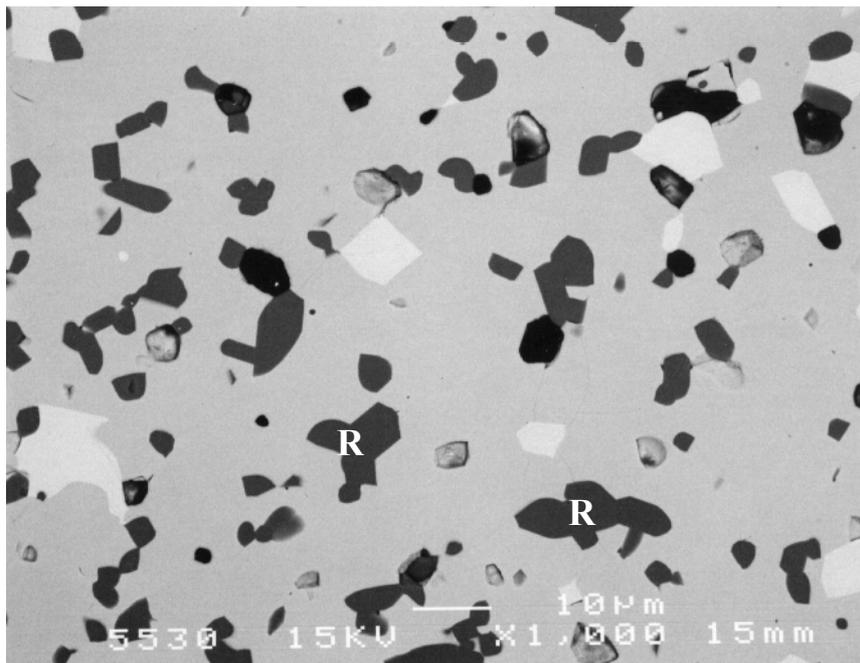
(b)

— 10 μm.

Figure G-10: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980392 (Task 1.2, composition B1-14, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The pellet consists of a matrix of pyrochlore (P), with some large Th/U-brannerite grains (B, light-grey - white) and porosity (A).



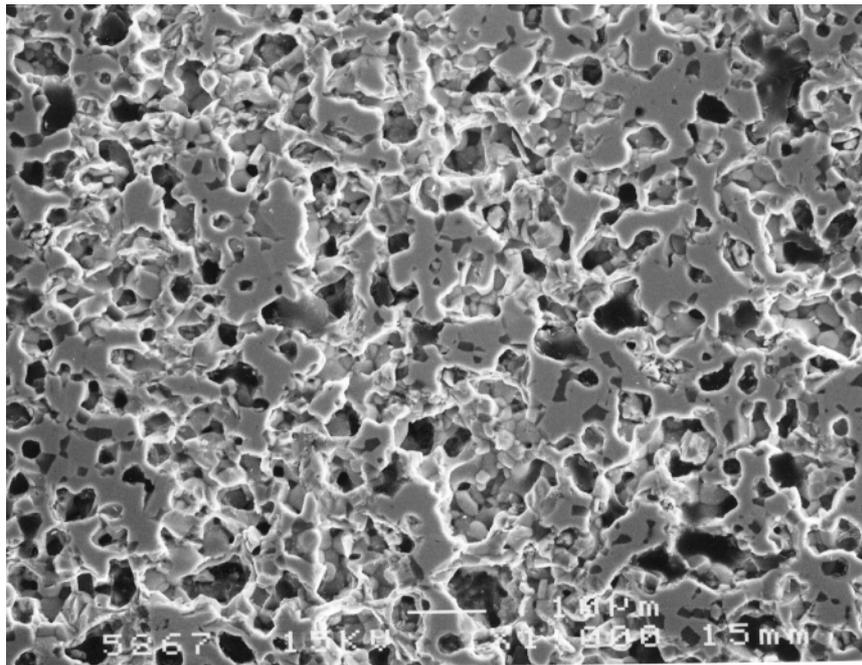
(a)



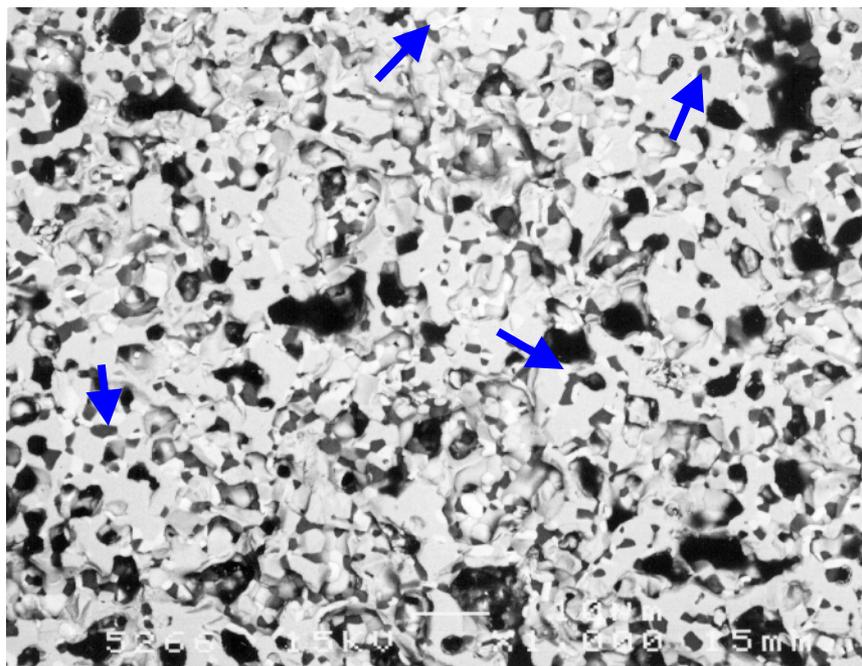
(b)

— 10 μm.

Figure G-11: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980397 (Task 1.2, composition B1-14, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The pellet consists of a matrix of pyrochlore (P), with Th/U-brannerite (B, light-grey), Hf-doped rutile (R, dark-grey) and porosity (A).

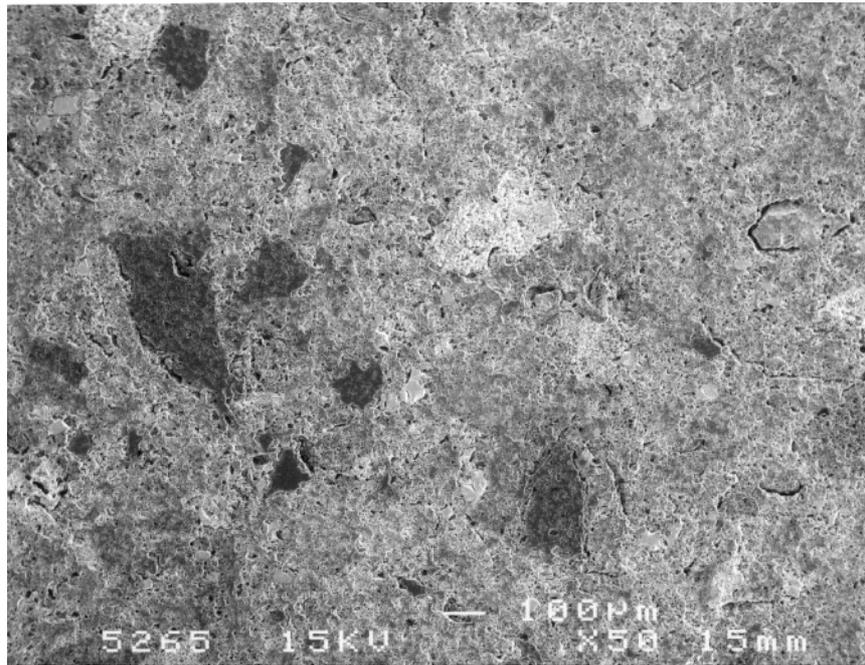


(a)

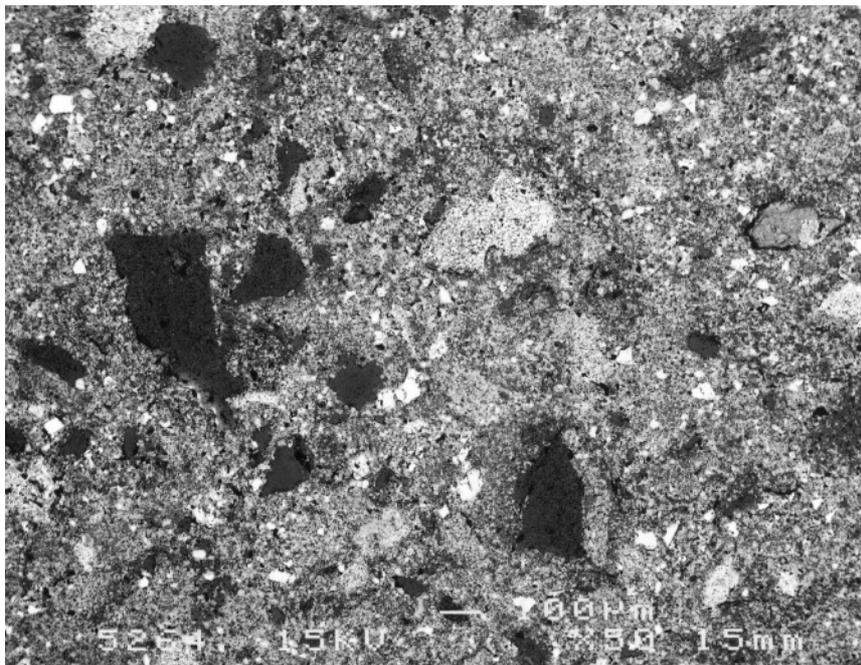


(b) — 10 μm.

Figure H-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980274 (Task 1.2, composition B1-16, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The sample is porous (see (a)). The matrix is pyrochlore, the light-grey phase is Th/U-brannerite (B) and the dark-grey phase is whitlockite (W).

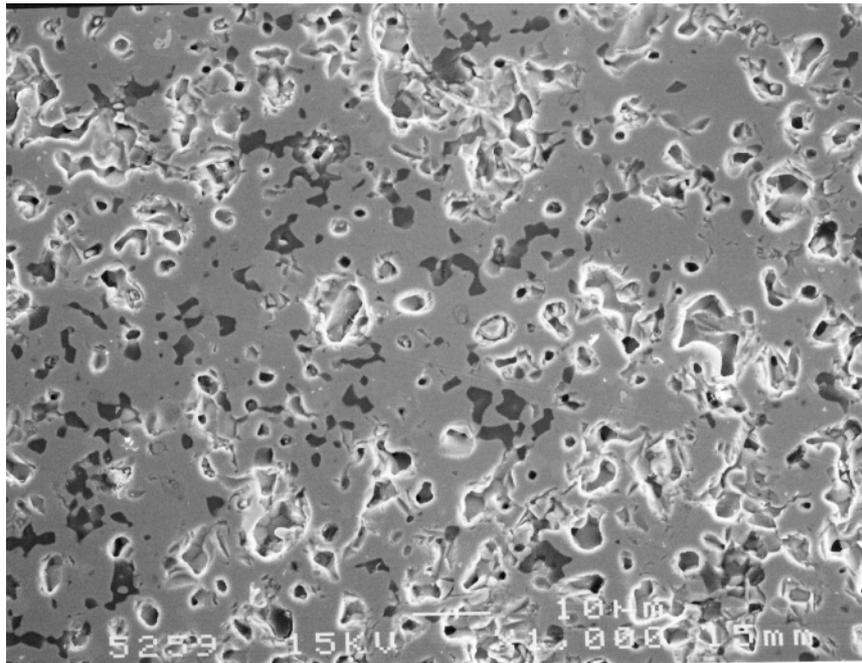


(a)

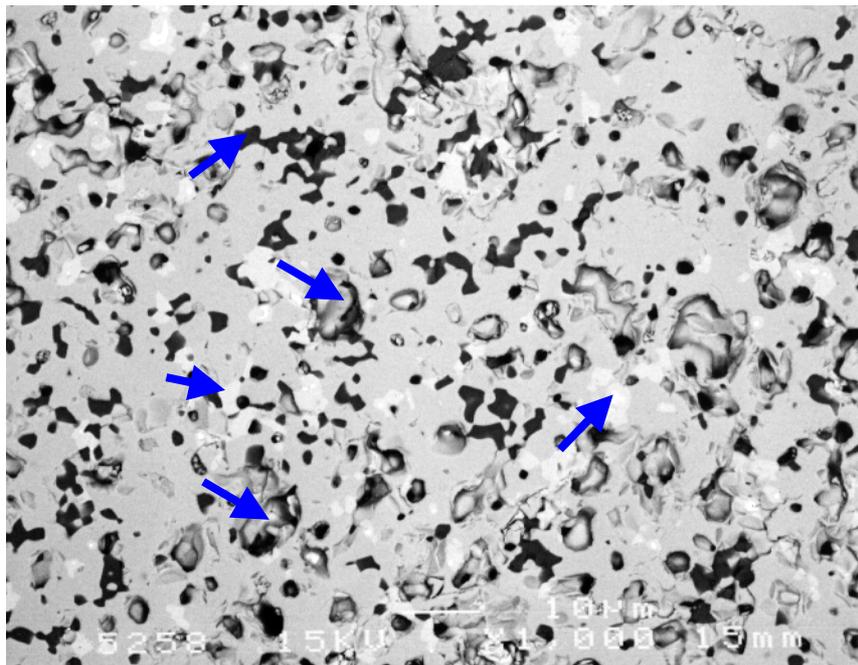


(b) — 100 μm.

Figure H-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980272 (Task 1.2, composition B1-16, oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The sample is porous (see (a)) and inhomogeneous. The major phases present are pyrochlore, zirconolite, brannerite, whitlockite,  $\text{UO}_2$ ,  $\text{ThO}_2$  and  $(\text{Th,U})\text{O}_2$ . A few grains of  $\text{HfO}_2$  were also detected.

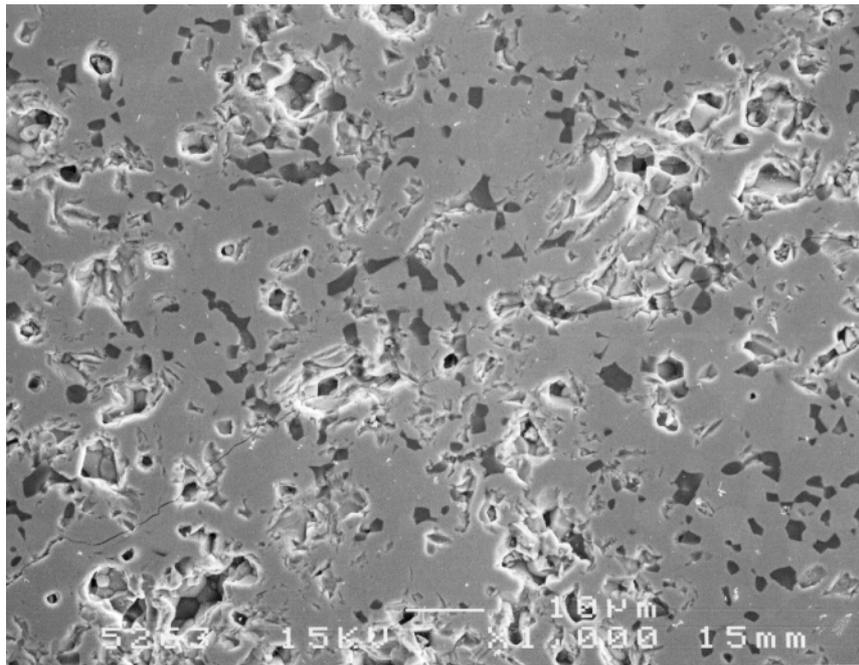


(a)

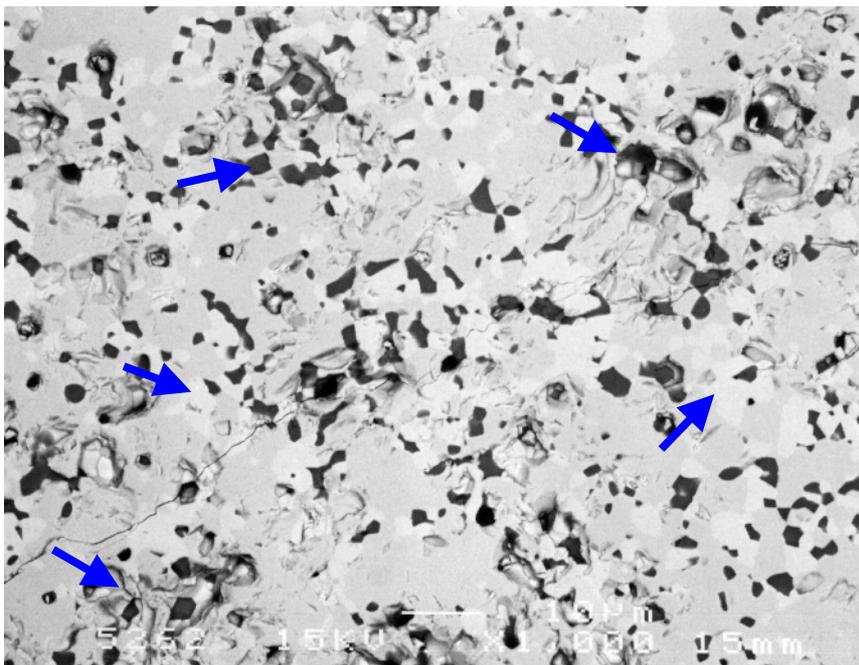


(b) — 10  $\mu\text{m}$ .

Figure H-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980270 (Task 1.2, composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore, with some brannerite (B, light grey grains) and whitlockite (W, dark-grey grains). Some (Th,U)O<sub>2</sub> (O, white spots in brannerite grains) and porosity (A) is also present.

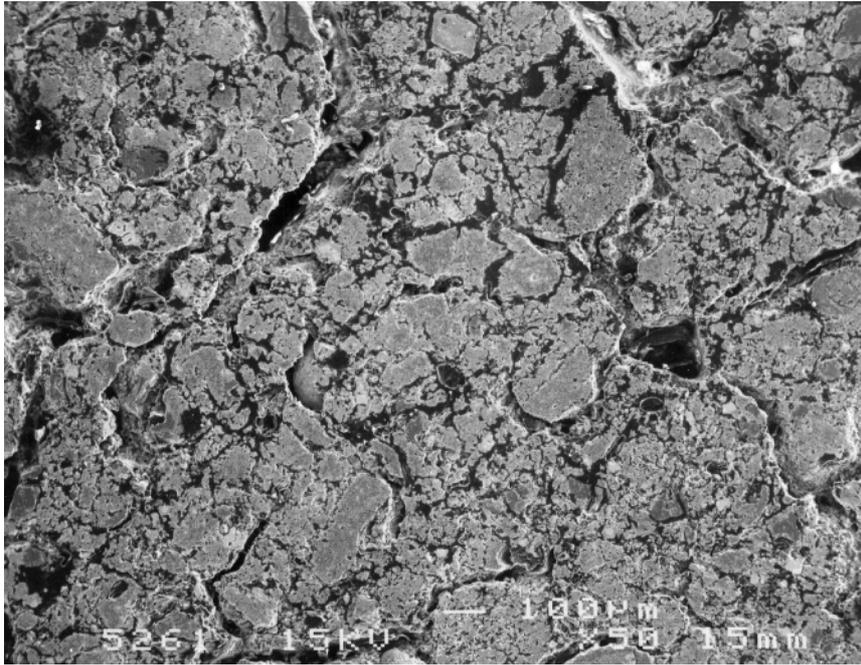


(a)



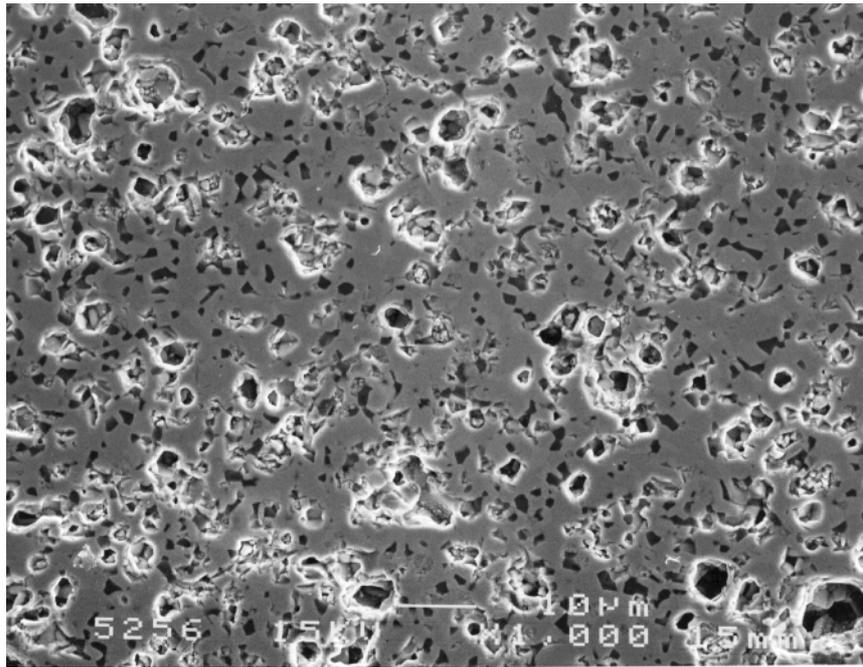
(b) — 10 μm.

Figure H-4: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980280 (Task 1.2, composition B1-16, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore, with some brannerite (B, light grey grains) and whitlockite (W, dark-grey grains). Porosity (A) is also present.

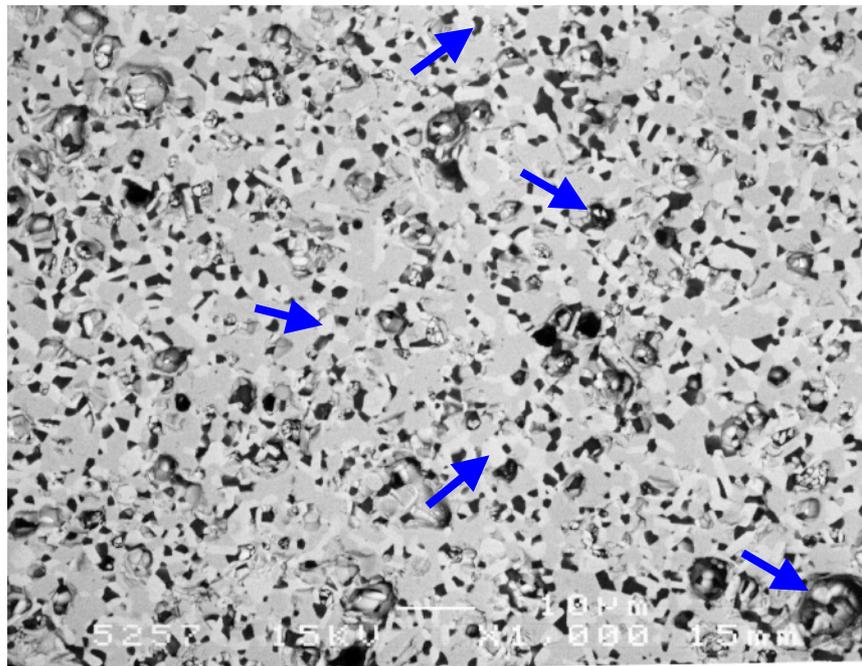


— 100 µm.

Figure H-5: Secondary electron micrograph of mws980278 (Task 1.2, composition B1-16, oxide-route, dry-milled 16 hours, sintered at 1350°C in air for 4 hours). The sample is very inhomogeneous, with large aggregates of variable composition.

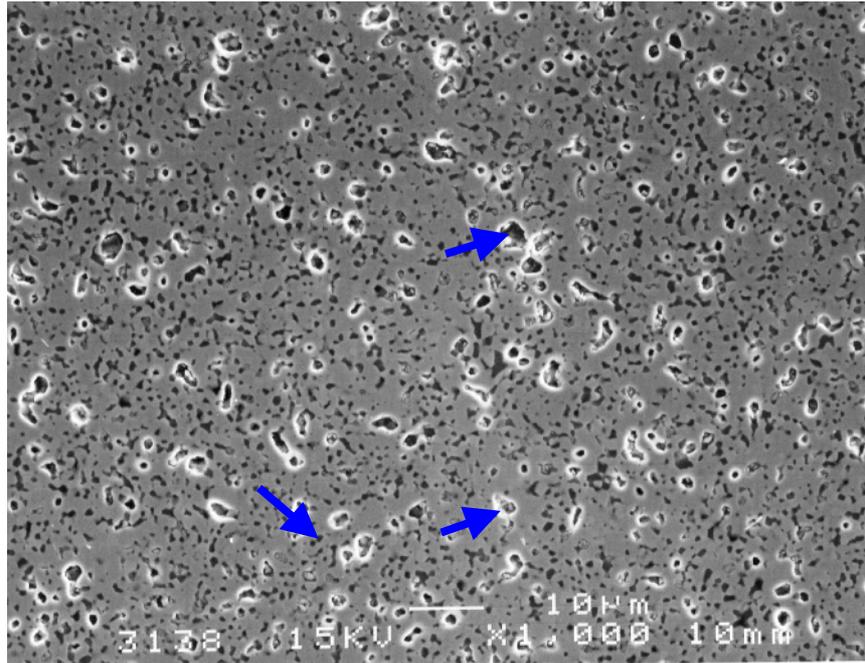


(a)

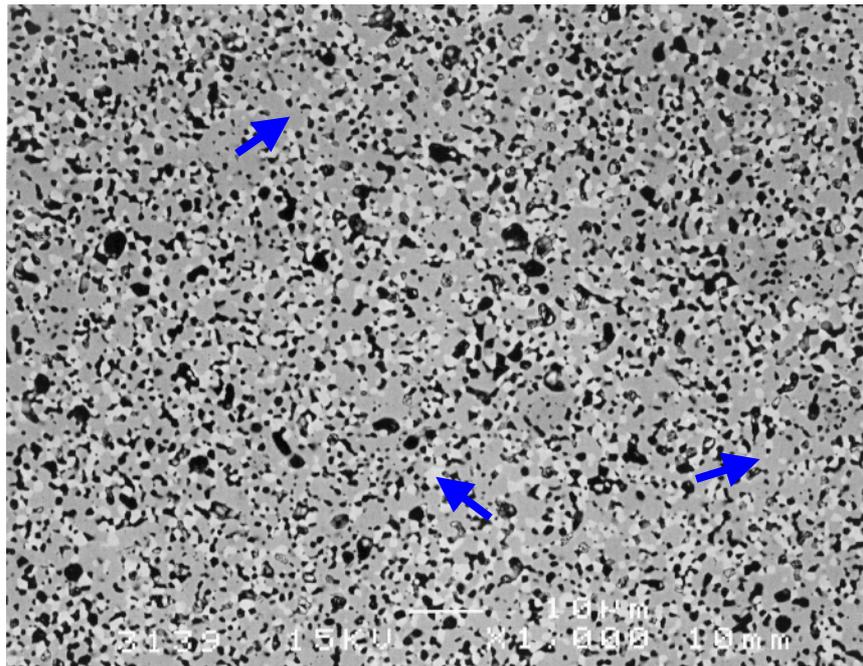


(b) — 10 μm.

Figure H-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980276 (Task 1.2, composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore, with brannerite (B, light grey grains) and whitlockite (W, dark-grey grains). Porosity (see (a)) is present.



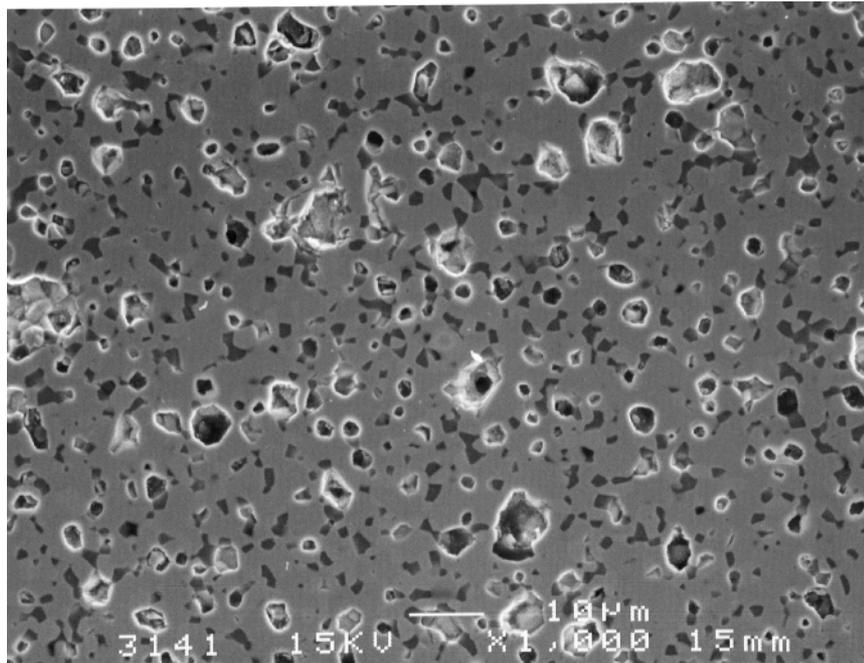
(a)



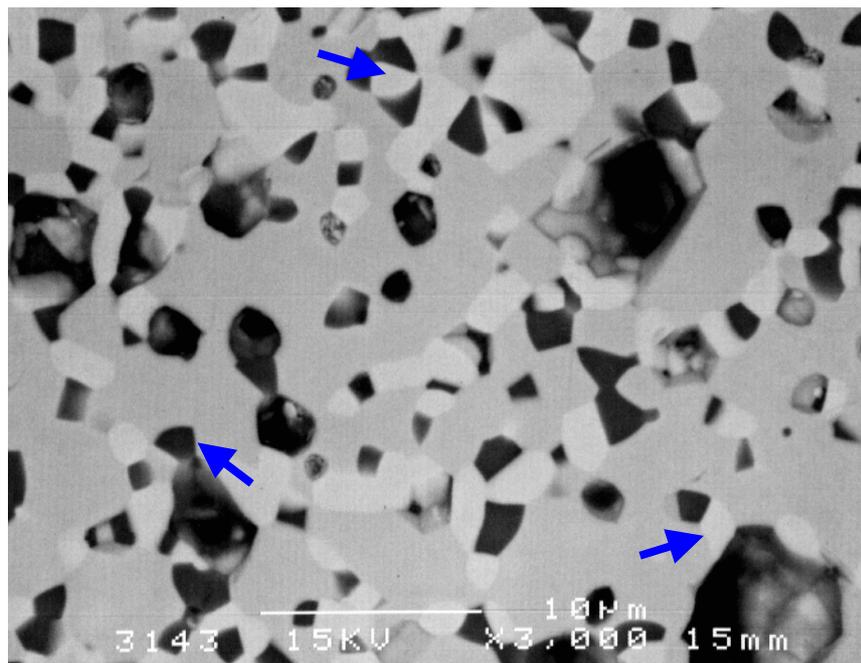
(b)

— 10 μm.

Figure H-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980321 (Task 1.2, composition B1-16, alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The pellet consists of a pyrochlore (P), with Th/U-brannerite (B, light-grey grains) and whitlockite (W, fine dark-grey grains). Pores (A) are also present.

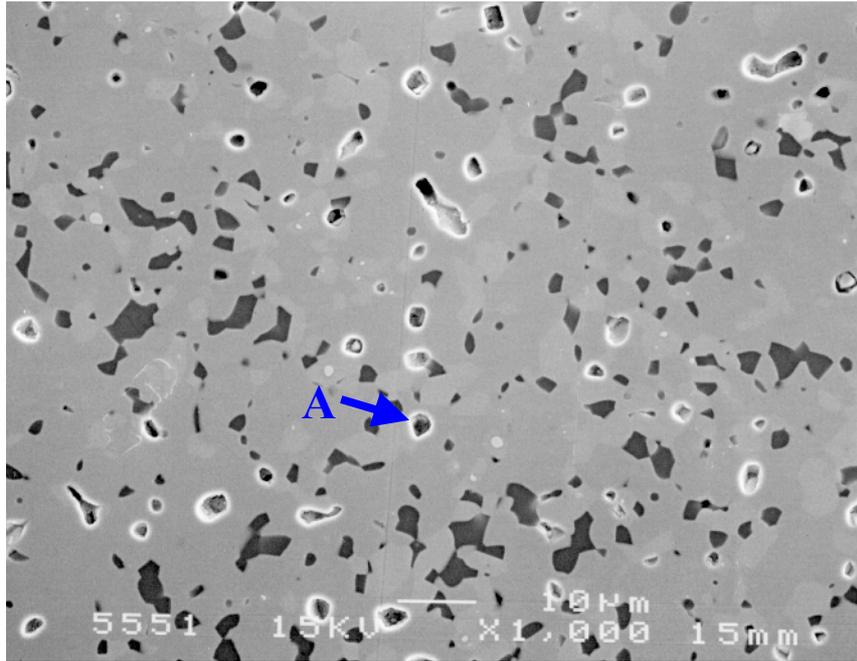


(a)

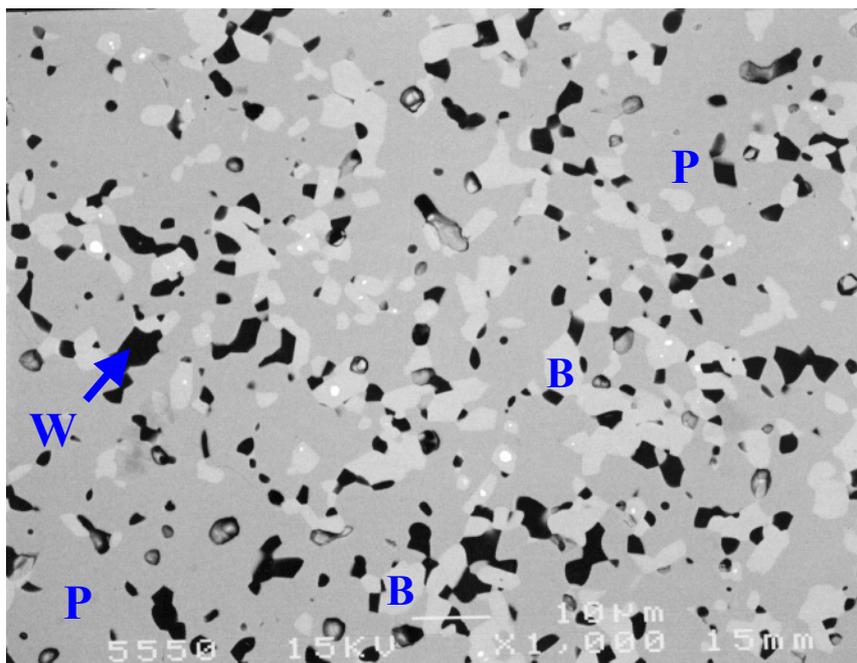


(b)  10 μm.

Figure H-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980307 (Task 1.2, composition B1-16, alkoxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The pellet consists of pyrochlore (P), with Th/U-brannerite (B, light-grey) grains and whitlockite (W, dark grey phase). Pores (A) are also present.



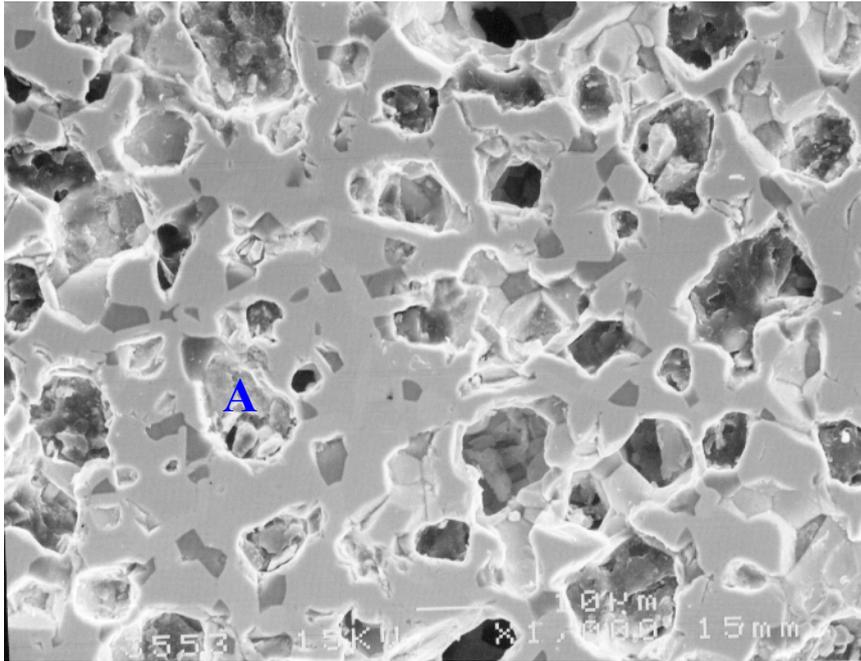
(a)



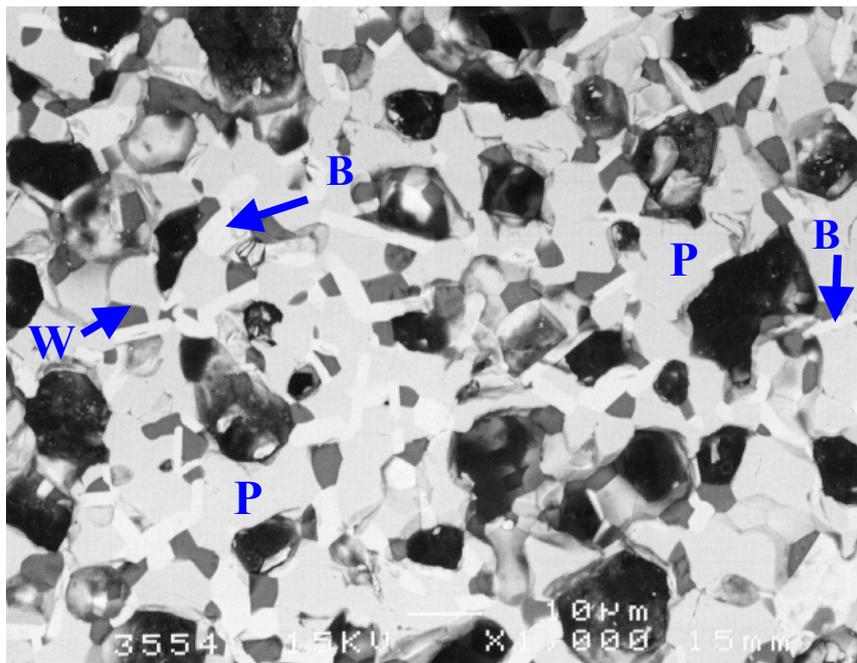
(b)

— 10 µm.

Figure H-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980412 (Task 1.2, composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours). The pellet consists of pyrochlore (P), with Th/U-brannerite (B, light-grey) grains and whitlockite (W, dark grey phase). Pores (A) are also present.



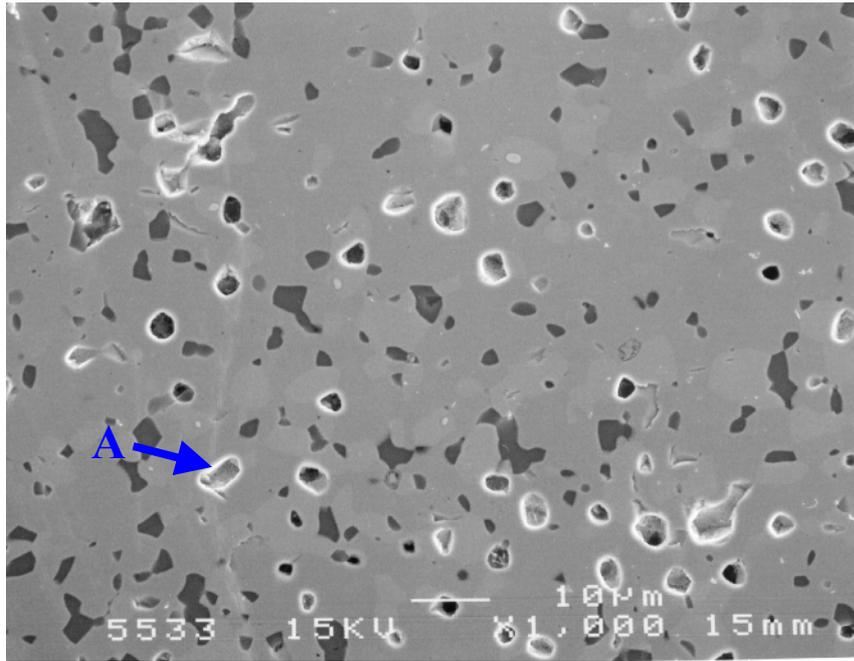
(a)



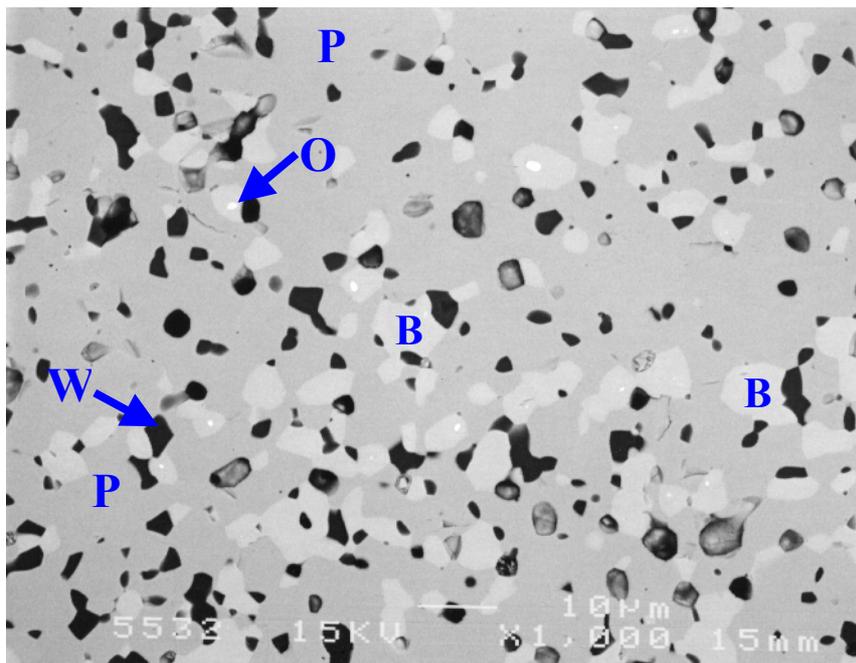
(b)

— 10 µm.

Figure H-10: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980393 (Task 1.2, composition B1-16, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The pellet consists of pyrochlore (P), with Th/U-brannerite (B) grains and whitlockite (W, dark grey phase). Pores (A) are also present.



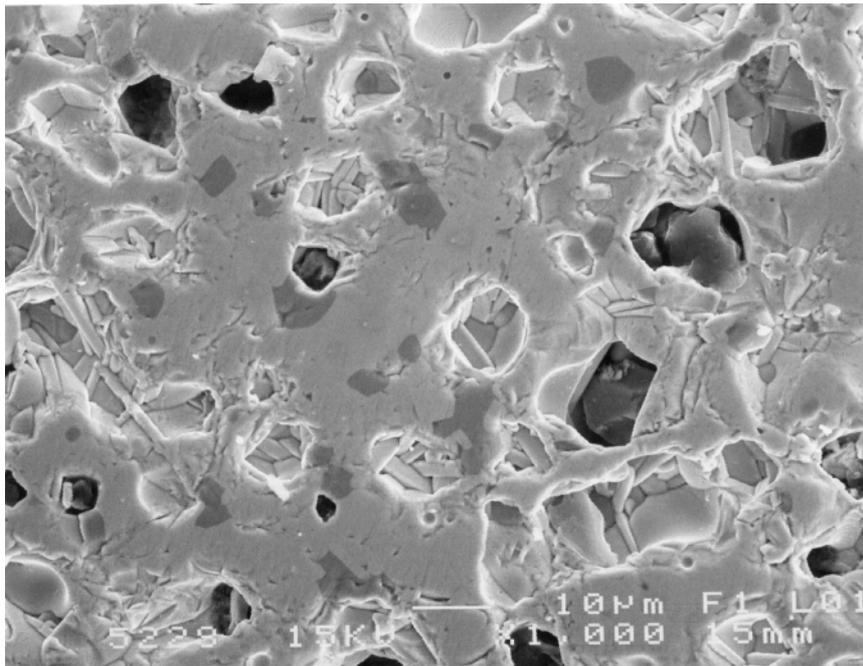
(a)



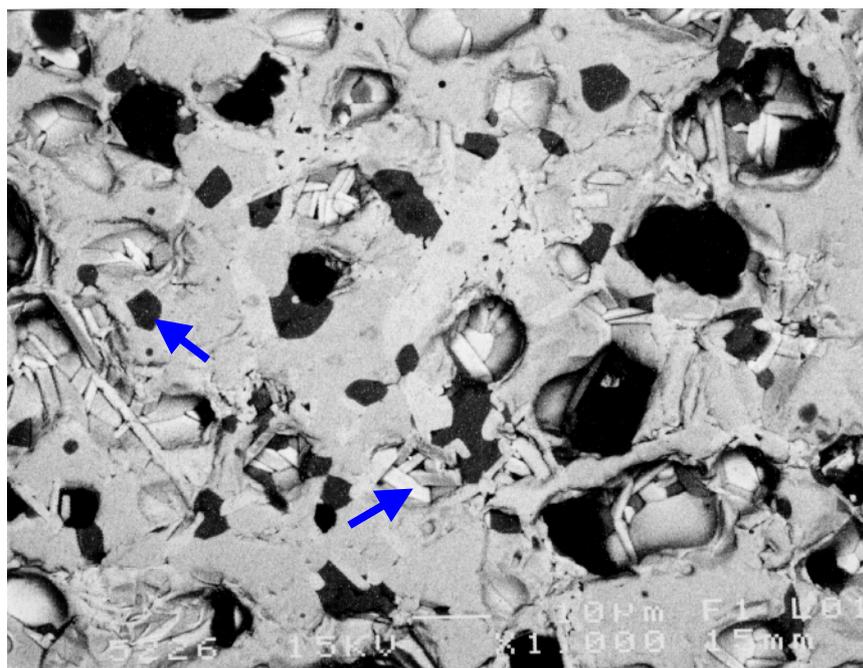
(b)

— 10 μm.

Figure H-11: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980398 (Task 1.2, composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours). The pellet consists of pyrochlore (P), with Th/U-brannerite (B) grains, whitlockite (W, dark grey phase) and some  $\text{UO}_2$  (O, white) located inside the brannerite grains. Pores (A) are also present.



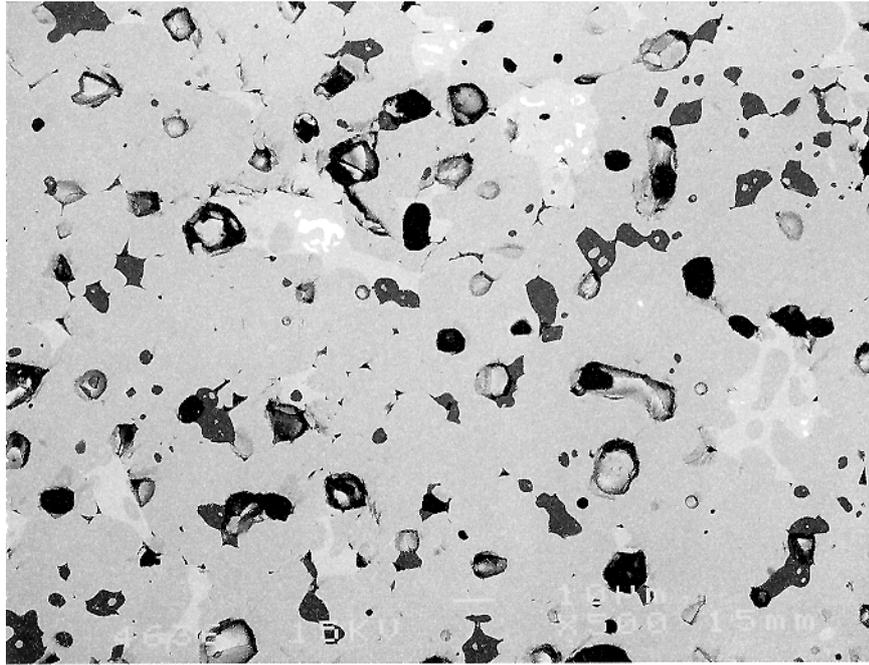
(a)



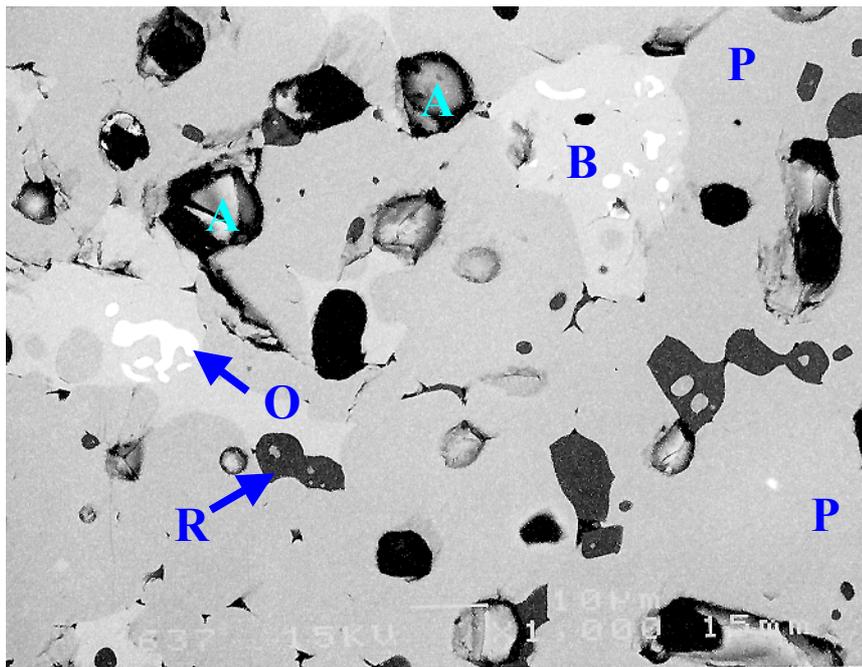
(b)

— 10 µm.

Figure I-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980293 (Pu92-01A) (Task 1.2, composition B1-1, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P), with Pu/U-brannerite (B) grains, Hf-doped rutile (R) and porosity (A).

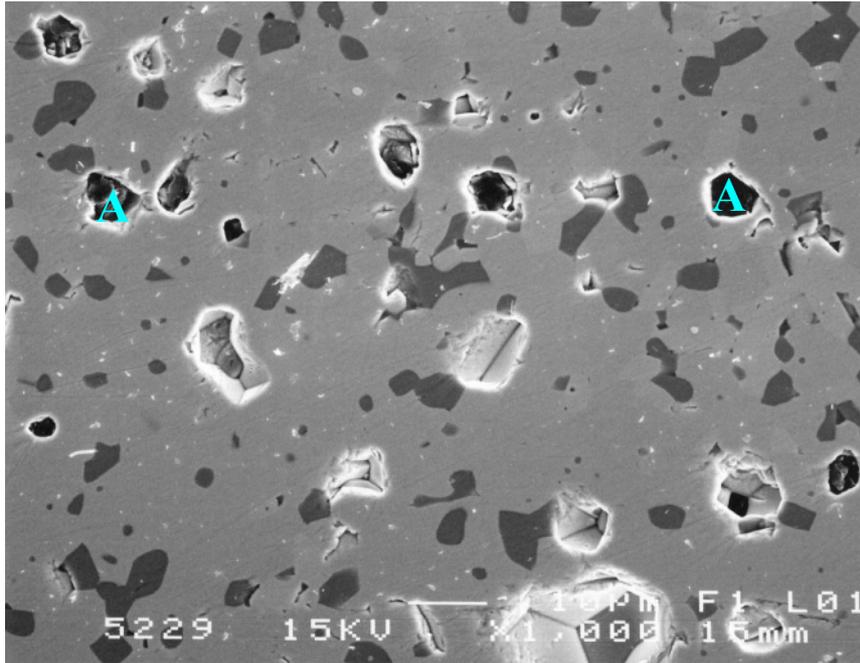


(a) — 10  $\mu\text{m}$ .

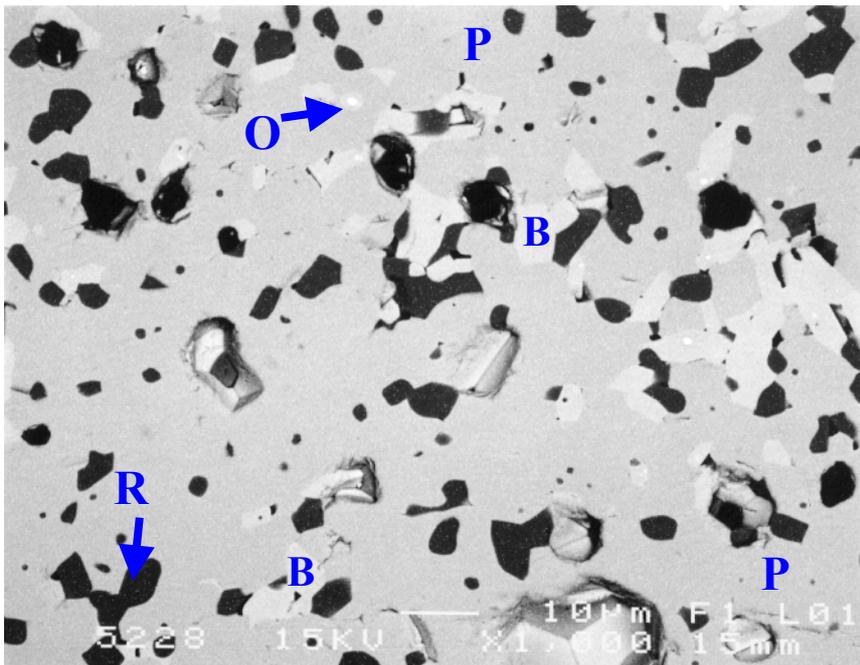


(b) — 10  $\mu\text{m}$ .

Figure I-2: (a) and (b) backscattered electron micrograph of Pu67 (Task 1.2, composition B1-1, oxide-route dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P), with Pu/U-brannerite (B) grains, Hf-doped rutile (R), PuO<sub>2</sub> (O, white) and porosity (A).



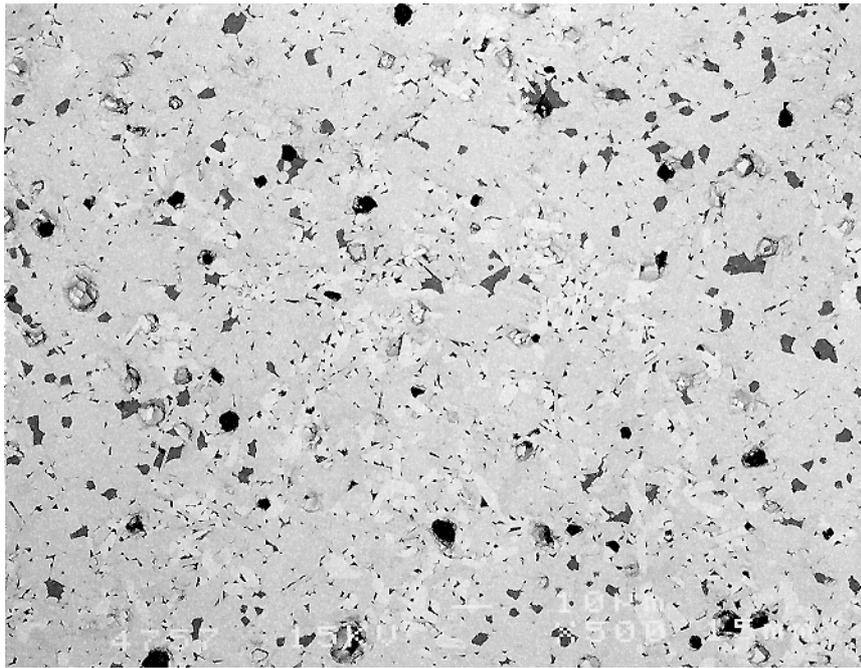
(a)



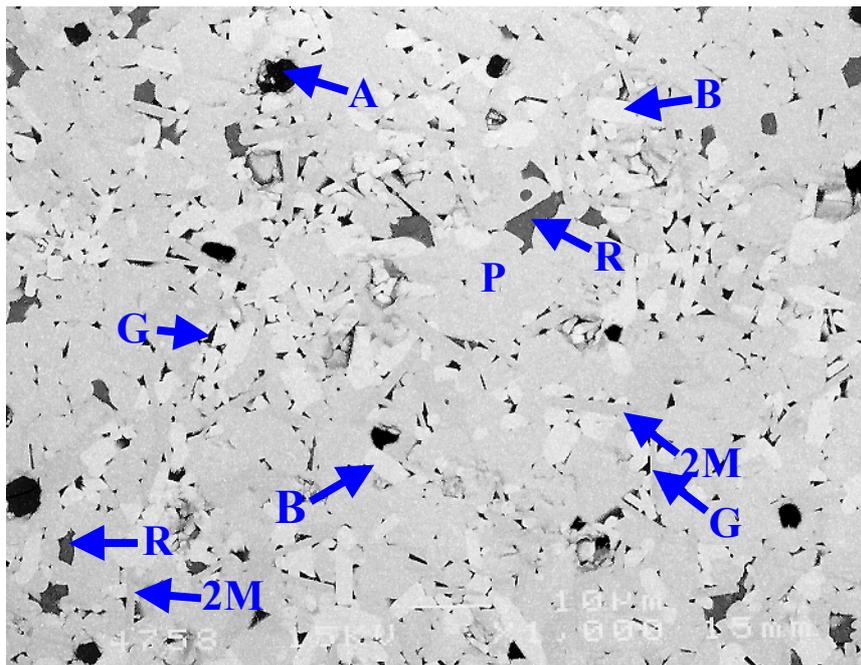
(b)

— 10 µm.

Figure I-3: (a) secondary electron micrograph and (b) backscattered electron micrograph of mws980199 (Pu88) (Task 1.2, composition B1-1, oxide-route wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P), with Pu/U-brannerite (B) grains, Hf-doped rutile (R), PuO<sub>2</sub> (O, white) and porosity (A).

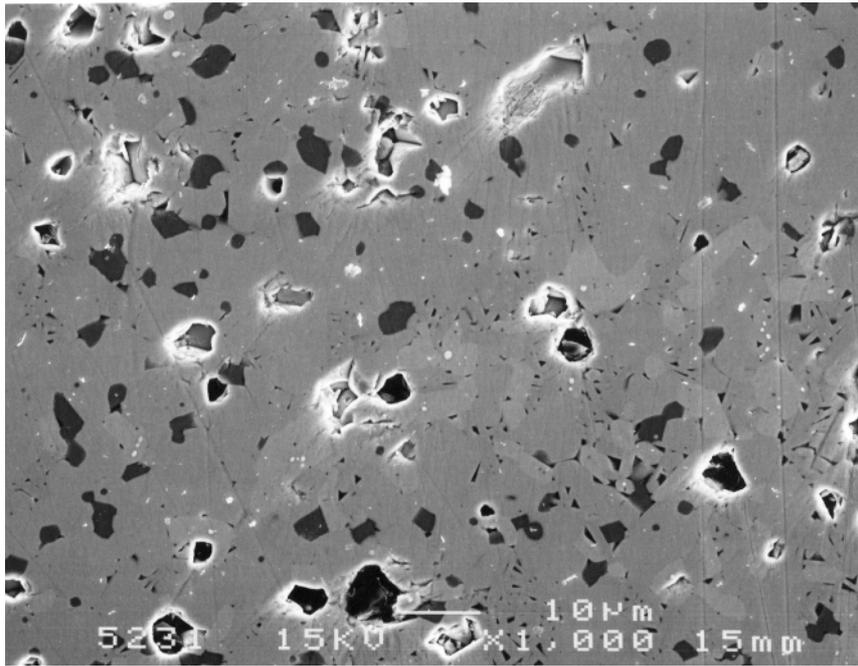


(a) — 10 μm.

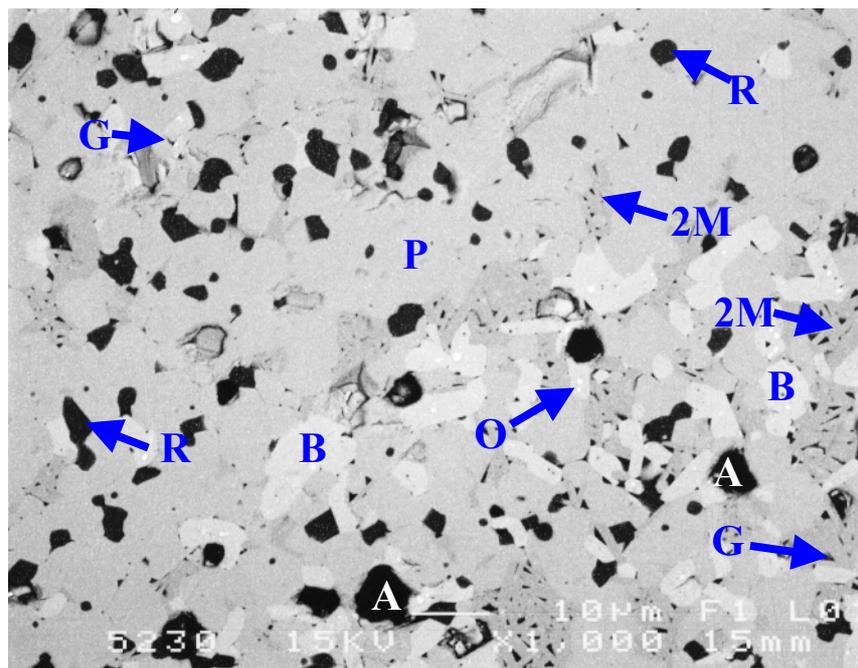


(b) — 10 μm.

Figure I-4: (a) and (b) backscattered electron micrograph of Pu73 (Task 1.2, composition B1-3 (A-9), alkoxide-route, wet-milled 16 hours, sintered at 1300°C in Ar for 4 hours). The pellet consists of a pyrochlore (P), 2M zirconolite (2M), Pu/U-brannerite (B), Hf-doped rutile (R), a silicate intergranular phase (G) and porosity (A).



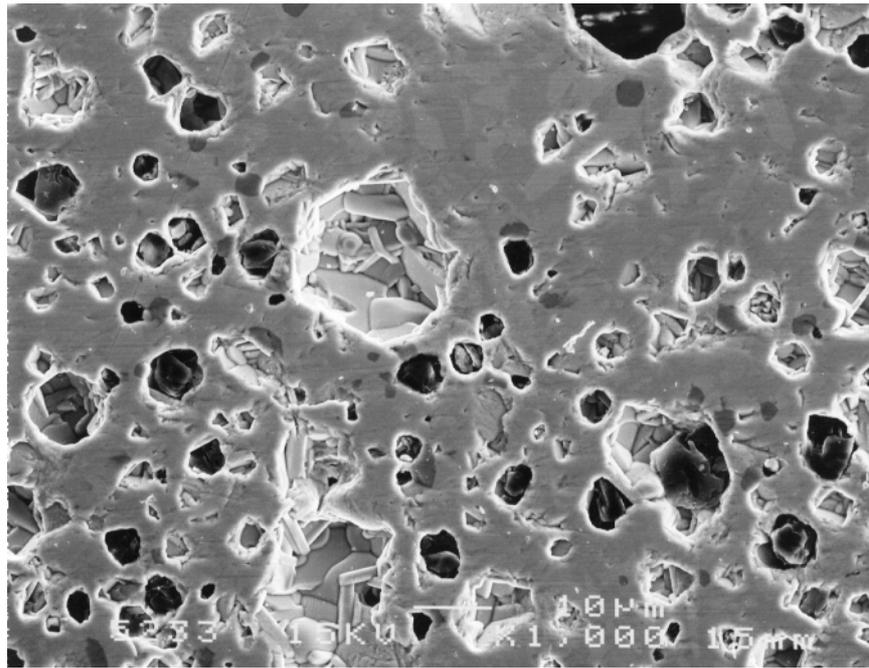
(a)



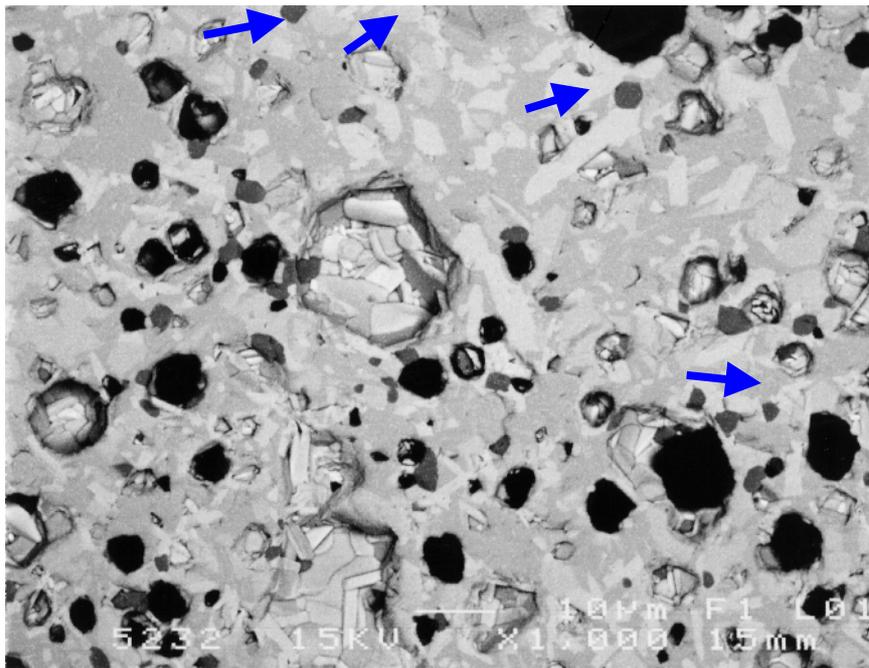
(b)

— 10 μm.

Figure I-5: (a) and (b) backscattered electron micrograph of mws980200 (Pu75) (Task 1.2, composition A-7, oxide-route wet-milled, sintered at 1325°C in Ar for 4 hours). The pellet consists of a pyrochlore (P), 2M zirconolite (2M), Pu/U-brannerite (B), Hf-doped rutile (R), a silicate intergranular phase (G), PuO<sub>2</sub> (O) and porosity (A).



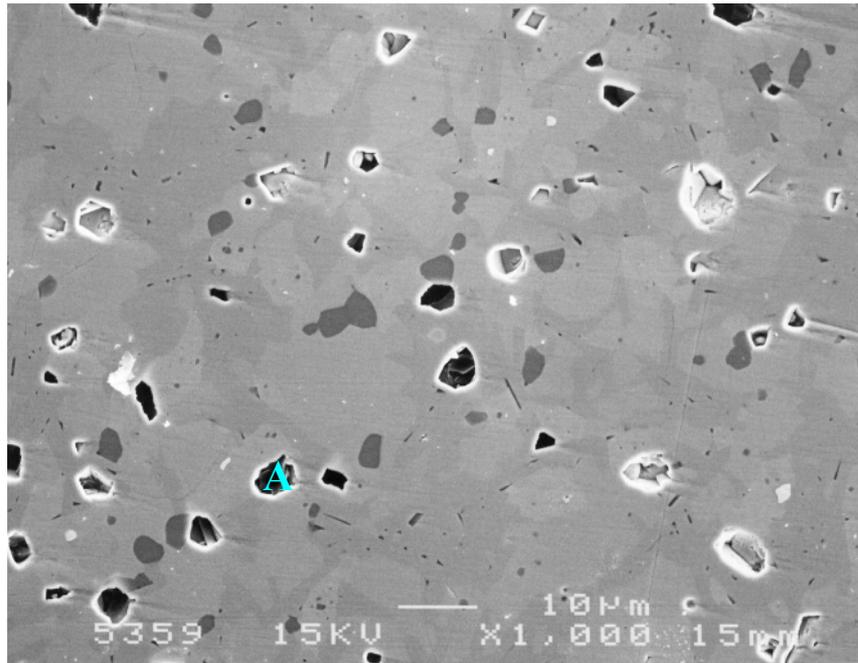
(a)



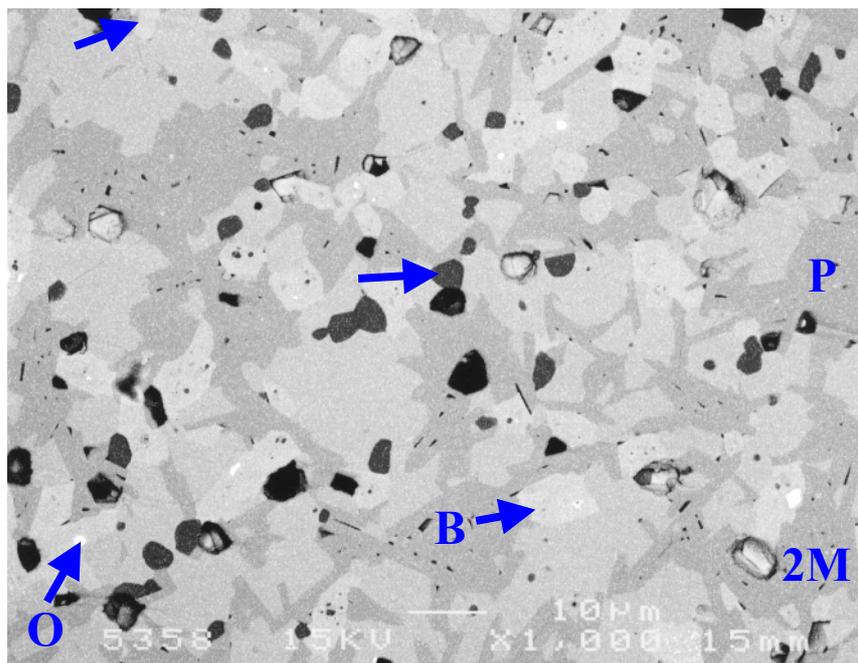
(b)

— 10 µm.

Figure I-6: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980294 (Pu093-01A) (Task 1.2, composition B1-9, alkoxide-route, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P, grey) and 2M zirconolite (2M, mid-grey), with Pu/U-brannerite (B, light-grey) grains, Hf-doped rutile (R) and porosity (A).



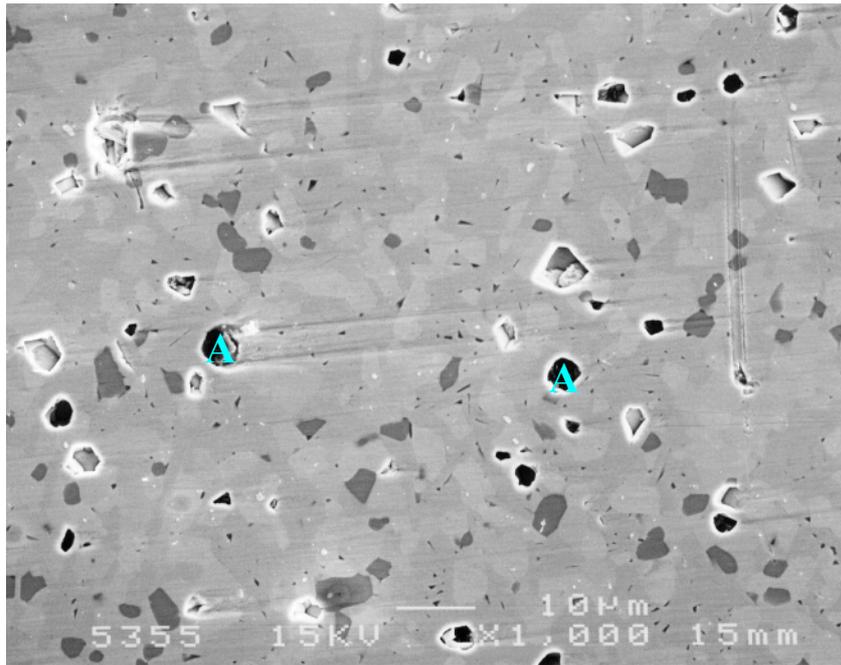
(a)



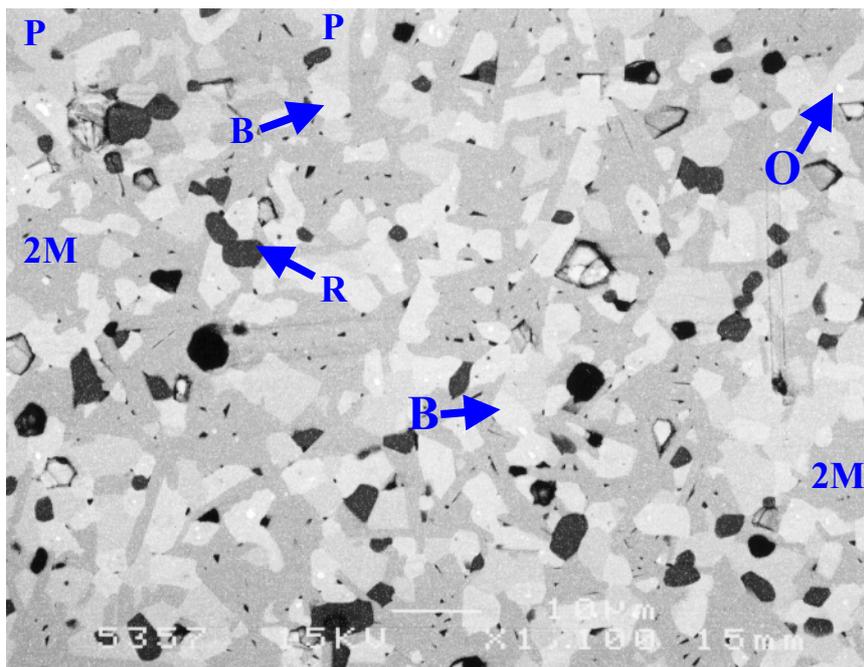
(b)

— 10 µm.

Figure I-7: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980353 (Pu098-01A) (Task 1.2, composition B1-9, oxide-route dry-milled, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P, grey) and 2M zirconolite (2M, mid-grey), with Pu/U-brannerite (B, light-grey) grains, Hf-doped rutile (R), PuO<sub>2</sub> (O, white) and porosity (A).



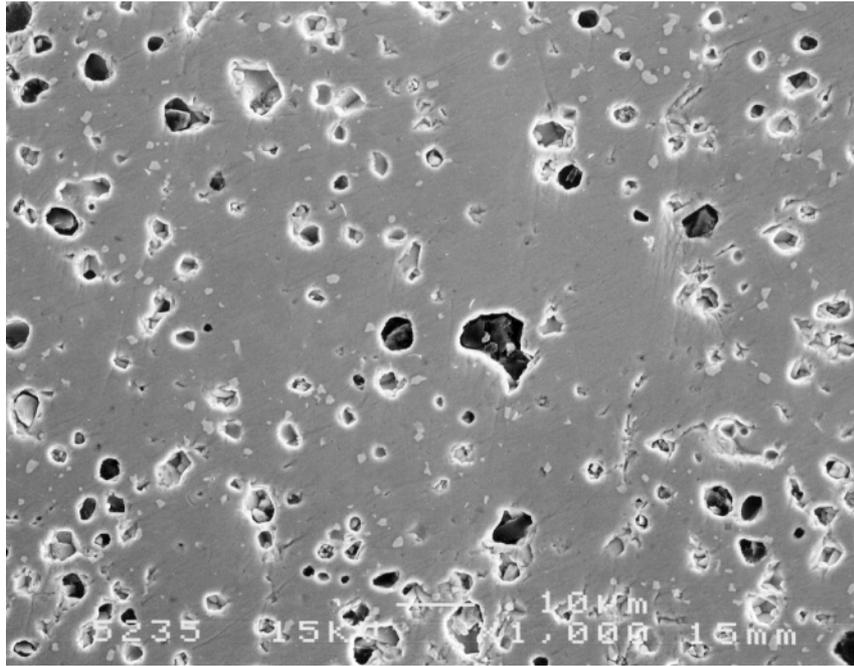
(a)



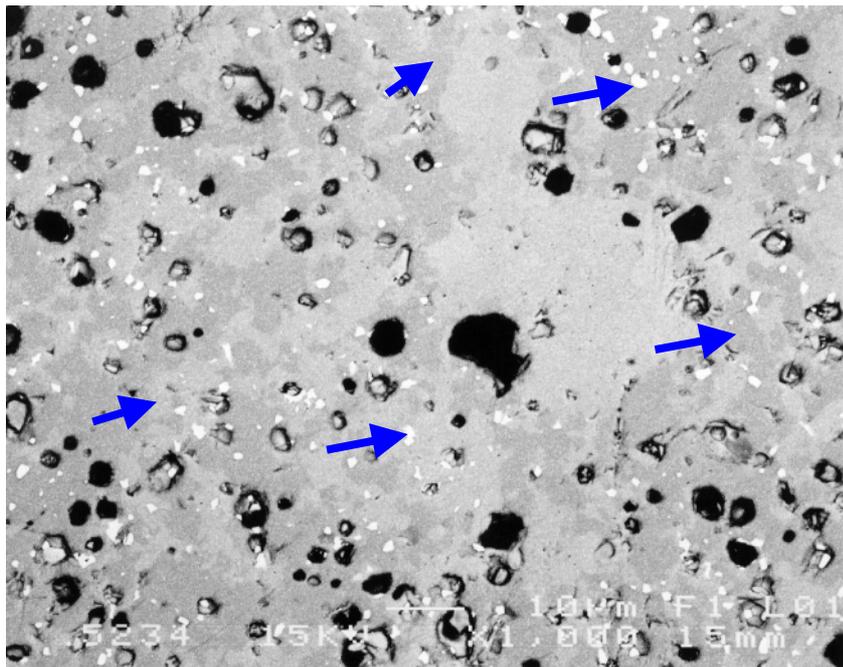
(b)

— 10 μm.

Figure I-8: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980352 (Pu097-01A) (Task 1.2, composition B1-9, oxide-route wet-milled, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P, grey) and 2M zirconolite (2M, mid-grey), with Pu/U-brannerite (B, light-grey) grains, Hf-doped rutile (R), PuO<sub>2</sub> (O, white) and porosity (A).



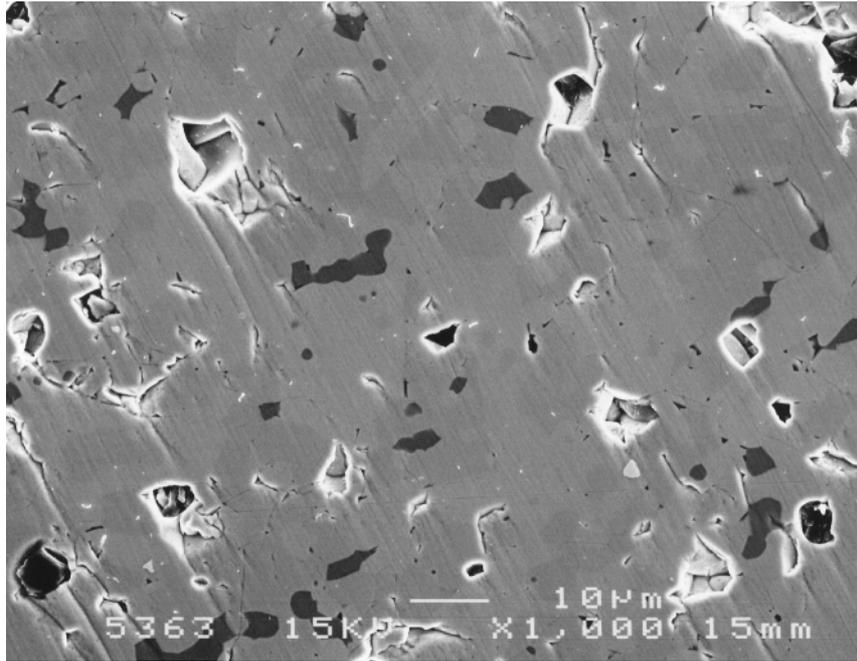
(a)



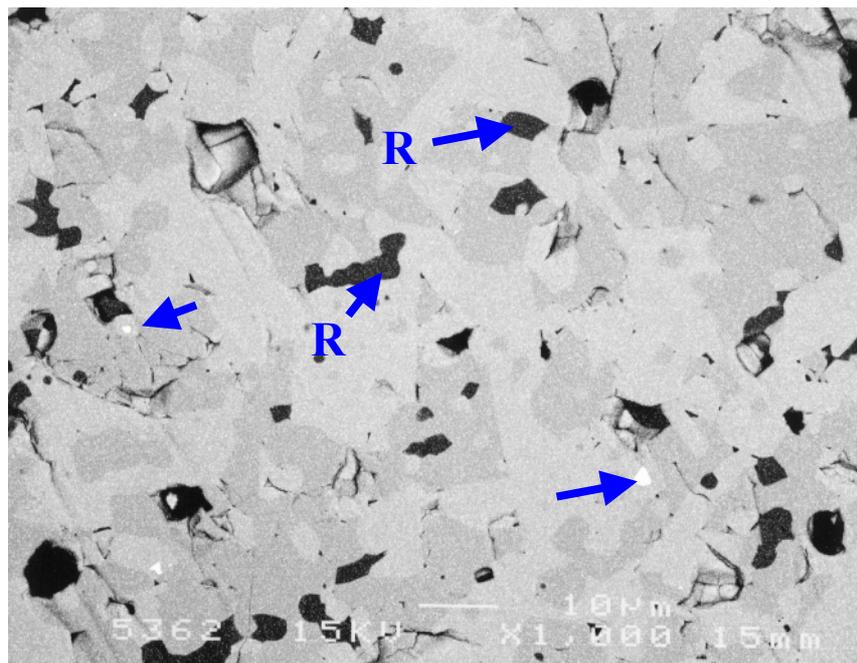
(b)

— 10 μm.

Figure I-9: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980295 (Pu094-01A) (Task 1.2, composition B1-11, alkoxide-route, sintered at 1350°C in Ar for 4 hours). The pellet matrix consists of a mixture of pyrochlore (P, grey) and Pu/U-brannerite (B, lightest grey, in matrix), some (Pu,U)O<sub>2</sub> (O, white) and porosity (A).



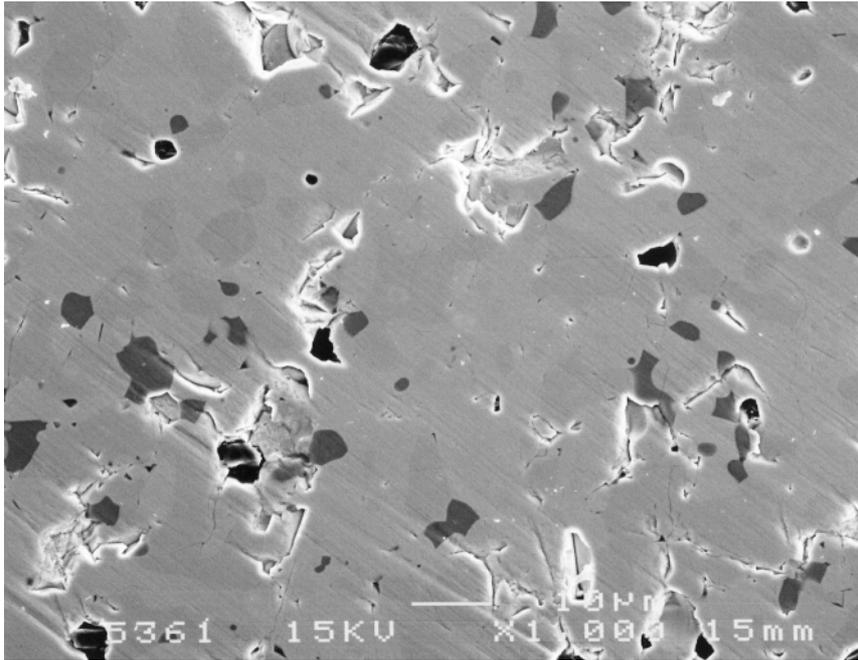
(a)



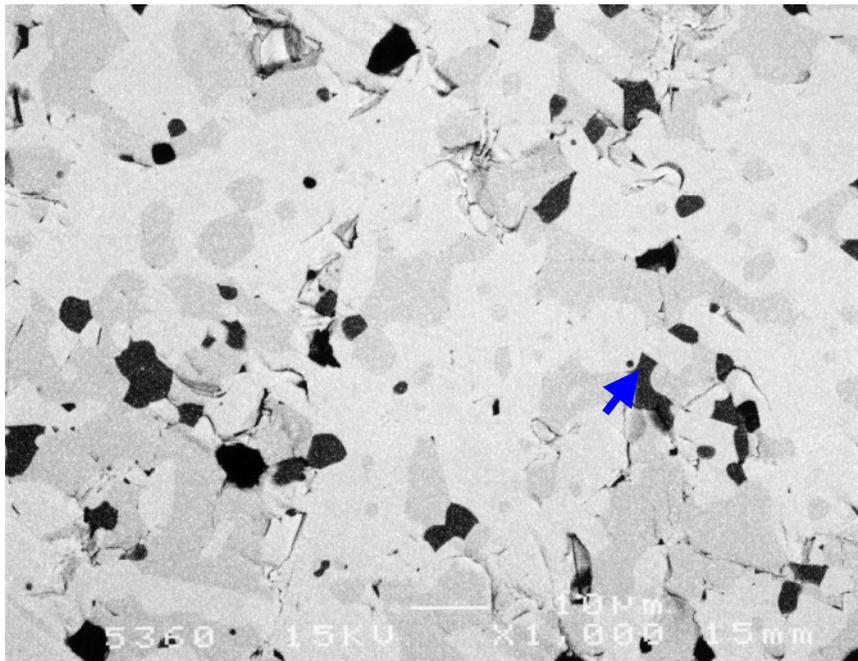
(b)

— 10 µm.

Figure I-10: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980355 (Pu100-01A) (Task 1.2, composition B1-11, oxide-route dry milled, sintered at 1350°C in Ar for 4 hours). The pellet matrix consists of a mixture of pyrochlore (P, grey) and Pu/U-brannerite (B, lightest grey, in matrix). Hf-doped rutile (R, dark-grey), some (Pu,U)O<sub>2</sub> (O, white) and porosity (A) are also present.



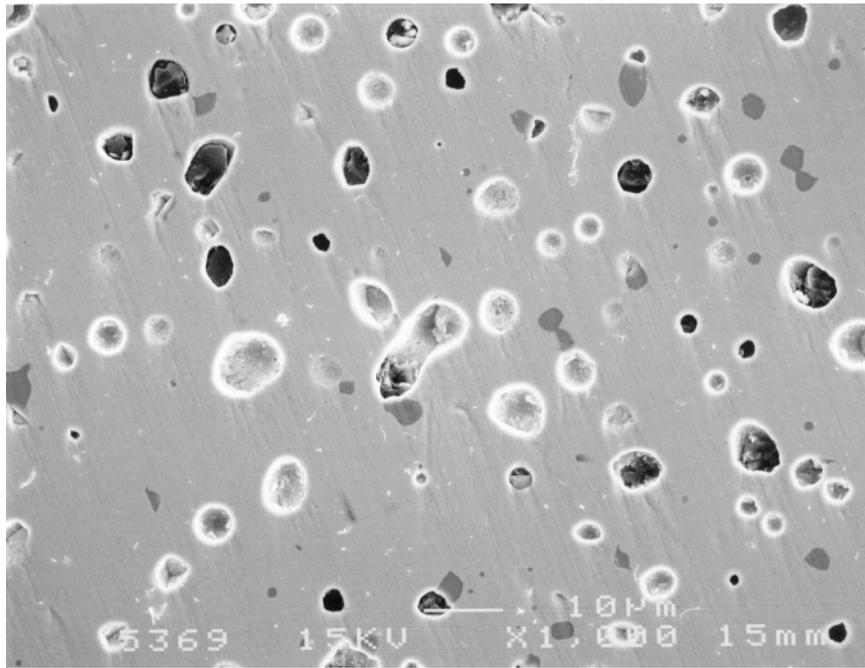
(a)



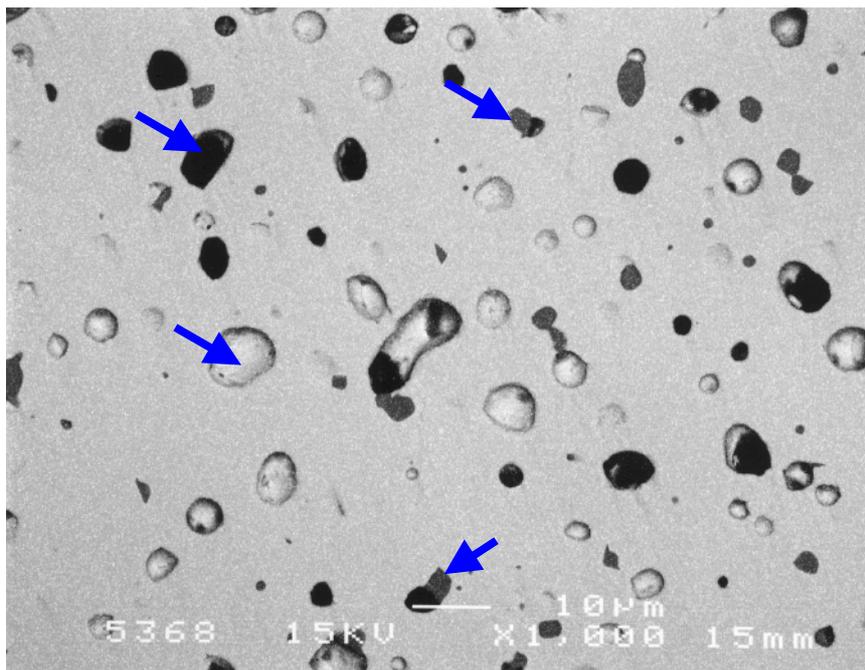
(b)

— 10  $\mu$ m.

Figure I-11: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980354 (Pu099-01A) (Task 1.2, composition B1-11, oxide-route wet milled, sintered at 1350°C in Ar for 4 hours). The pellet matrix consists of a mixture of pyrochlore (P, grey) and Pu/U-brannerite (B, lightest grey, in matrix). Hf-doped rutile (R, dark-grey), and porosity (A) are also present.

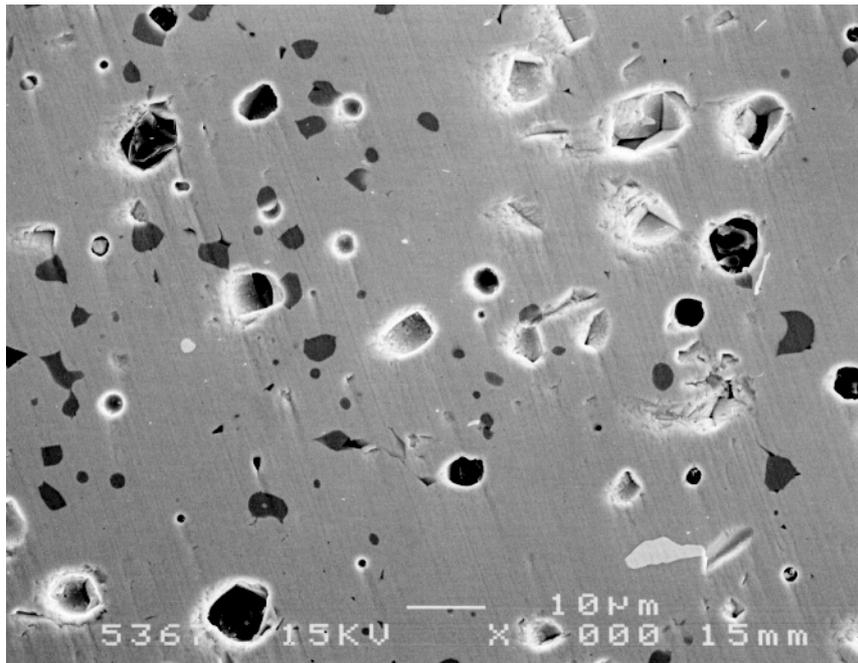


(a) — 10 µm.

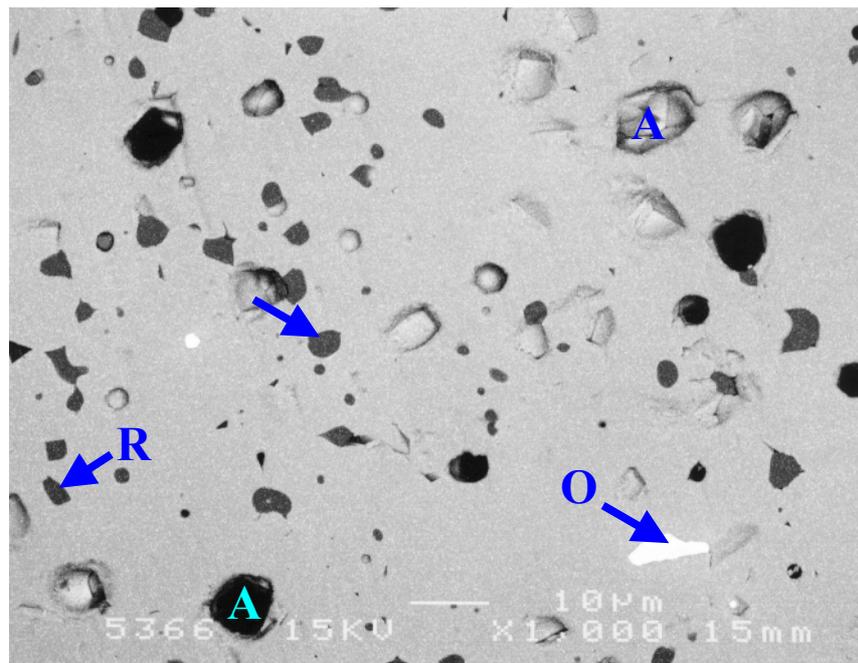


(b) — 10 µm.

Figure I-12: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980361 (Pu105-01A) (Task 1.2, composition B1-13 (~10 % (nominal) perovskite), alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the dark-grey phase is rutile (R). Porosity (A) is also present. No perovskite or brannerite was detected in this sample.

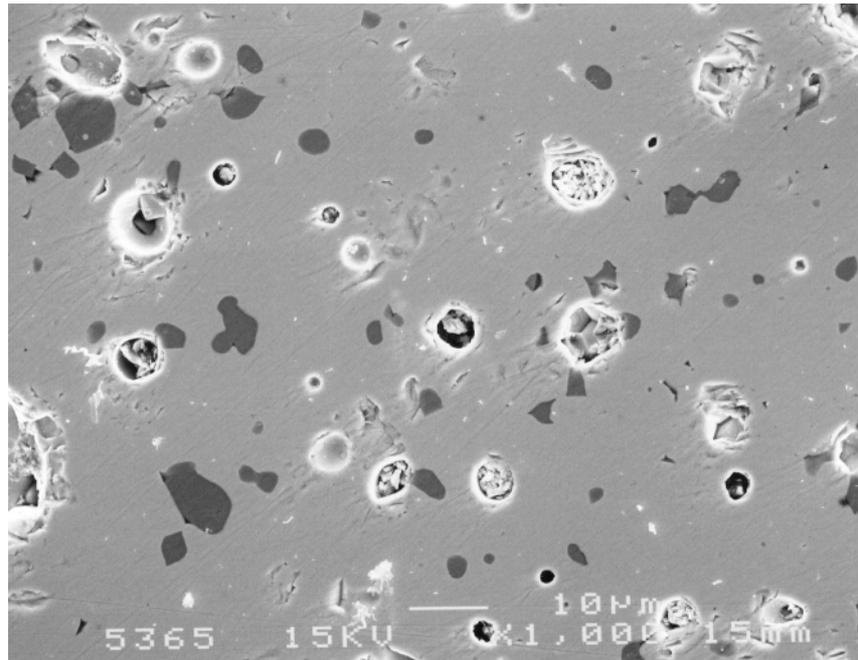


(a)

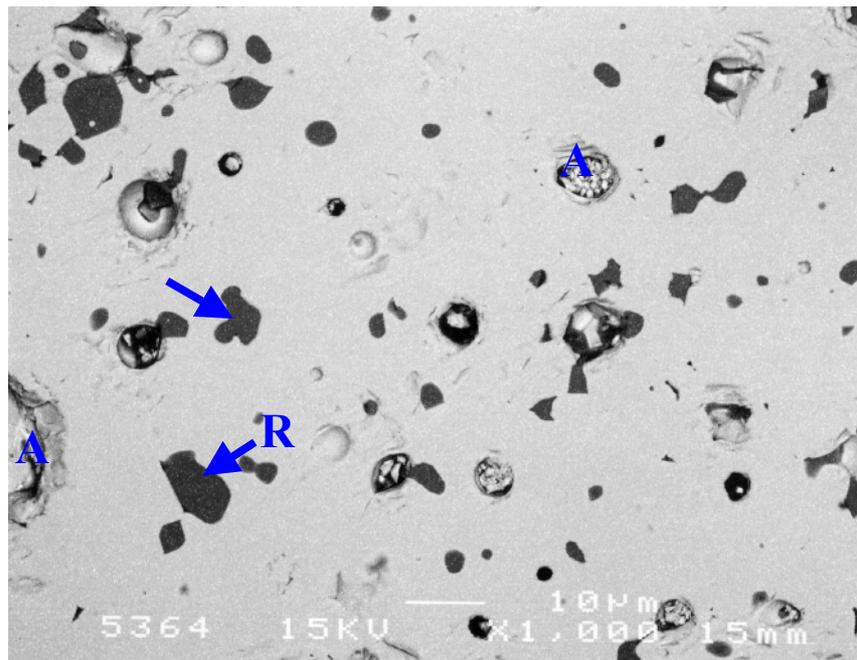


(b) — 10 μm.

Figure I-13: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980357 (Pu102-01A) (Task 1.2, composition B1-13 (~10 % (nominal) perovskite), oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the dark-grey phase is rutile (R) and the white phase is PuO<sub>2</sub> (O). Porosity (A) is also present. No perovskite or brannerite was detected in this sample.

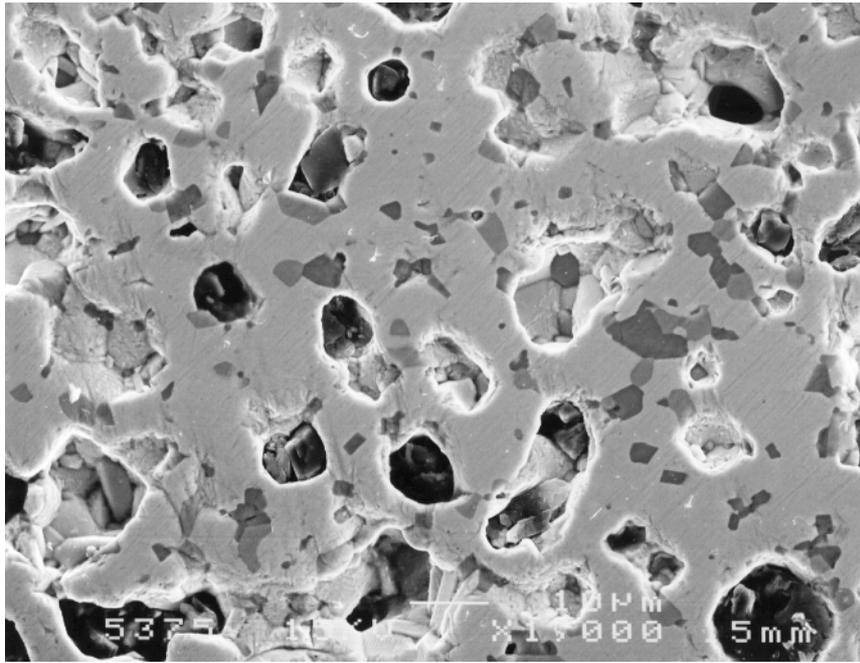


(a)

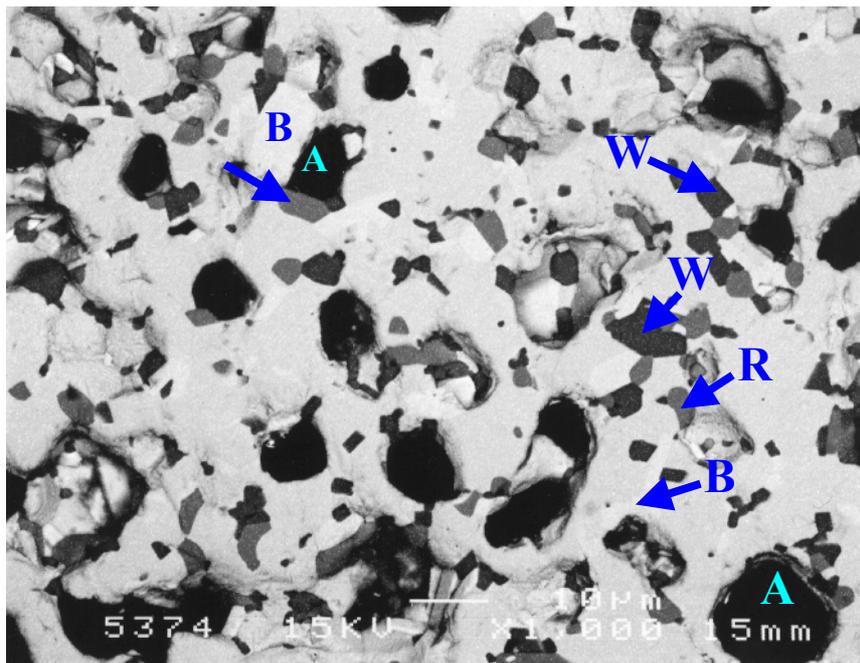


(b) — 10 µm.

Figure I-14: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980356 (Pu101-01A) (Task 1.2, composition B1-13 (~10 % (nominal) perovskite), oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore and the dark-grey phase is rutile (R). Porosity (A) is also present. No perovskite or brannerite was detected in this sample.

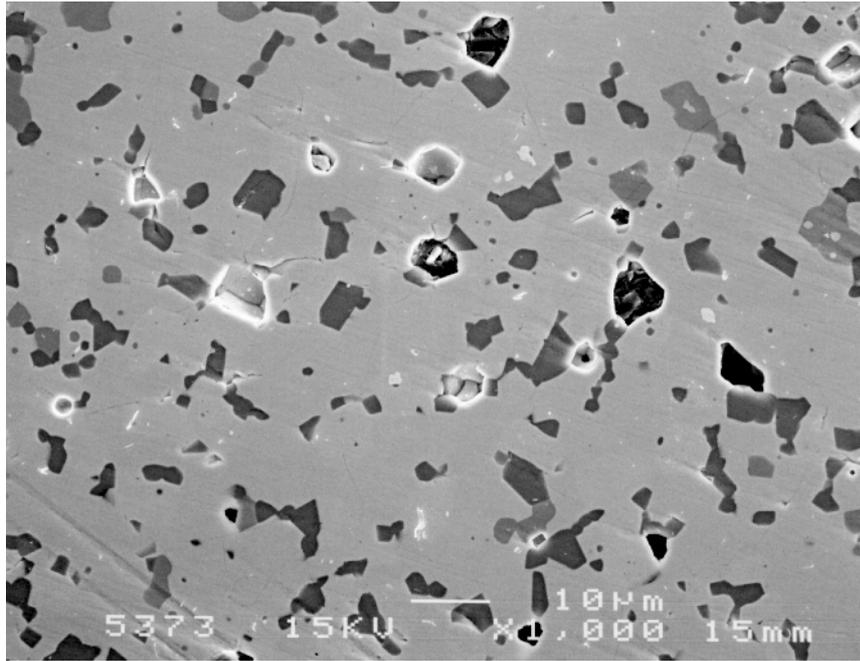


(a)

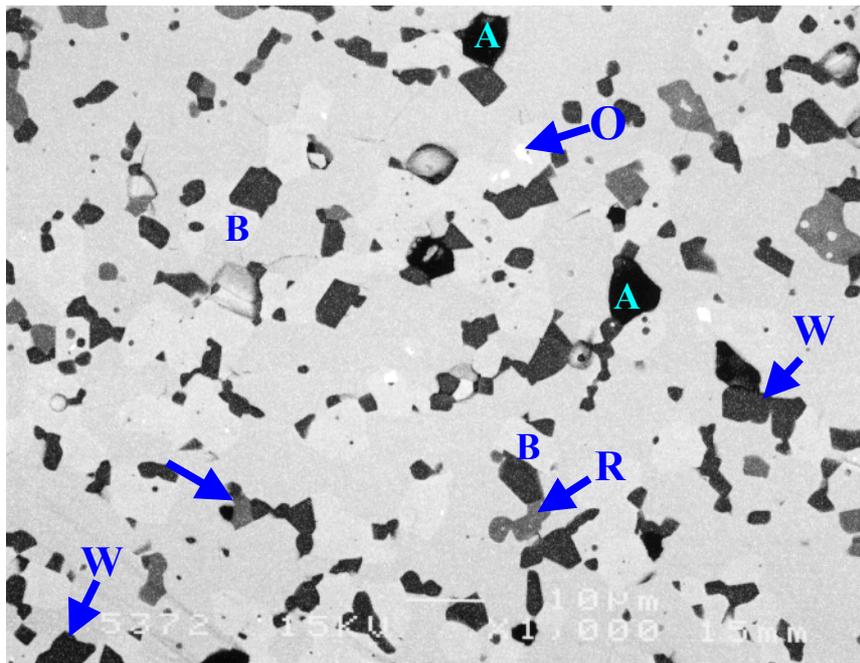


(b) — 10 μm.

Figure I-15: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980362 (Pu106-01A) (Task 1.2, composition B1-15 (~10 % (nominal) phosphate), alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the lighter grey phase is Pu/U-brannerite, the grey phase is rutile (R) and the dark-grey phase is whitlockite (W). Porosity (A) is also present.

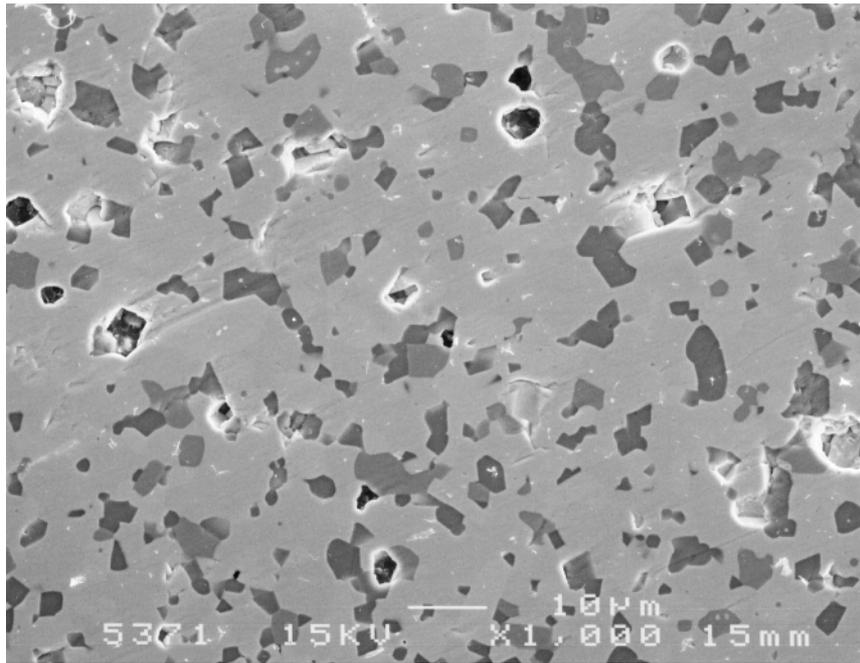


(a)

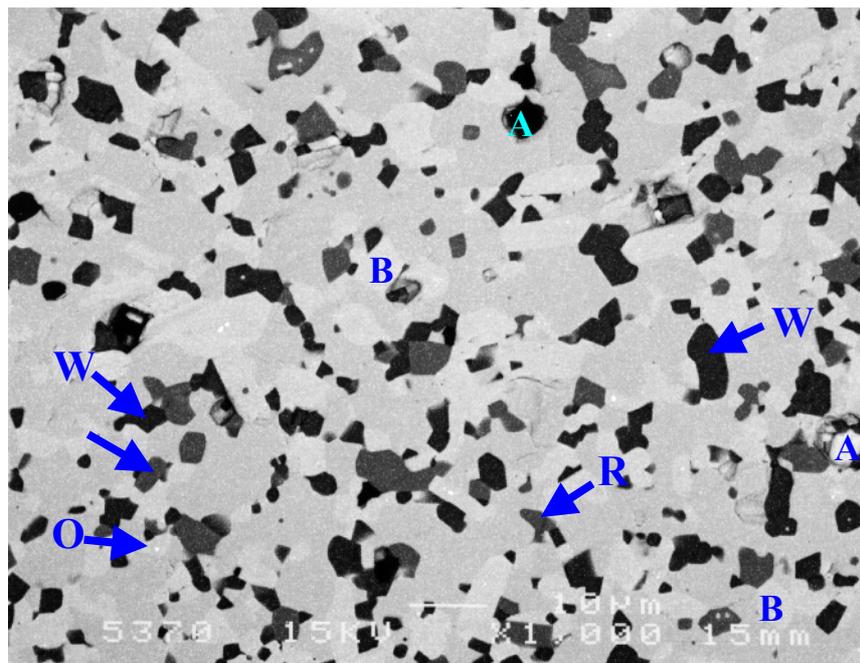


(b) — 10 μm.

Figure I-16: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980359 (Pu104-01A) (Task 1.2, composition B1-15 (~10 % (nominal) phosphate), oxide-route, dry-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the lighter grey phase is Pu/U-brannerite, the grey phase is rutile (R) and the dark-grey phase is whitlockite (W). Porosity (A) and PuO<sub>2</sub> (O) are also present.

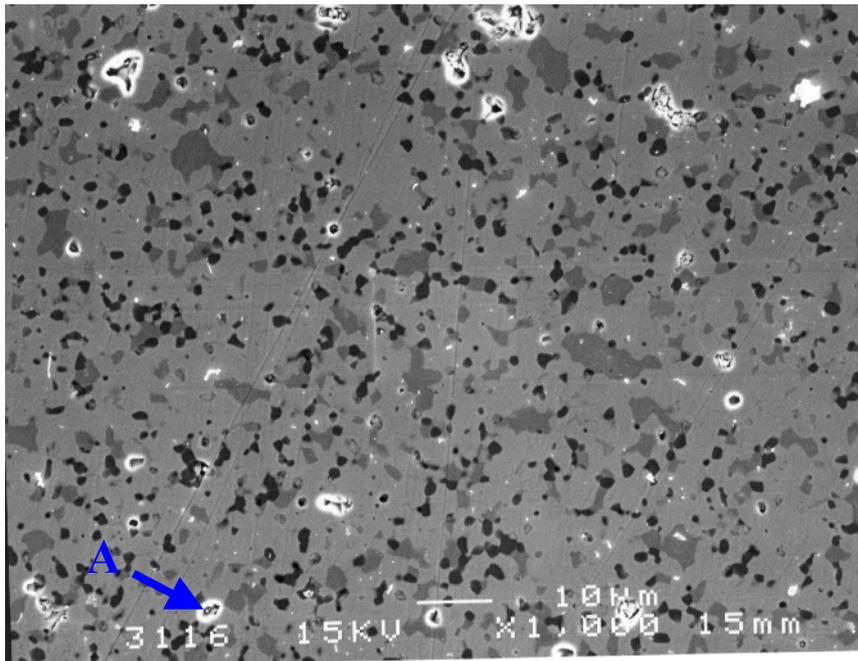


(a)

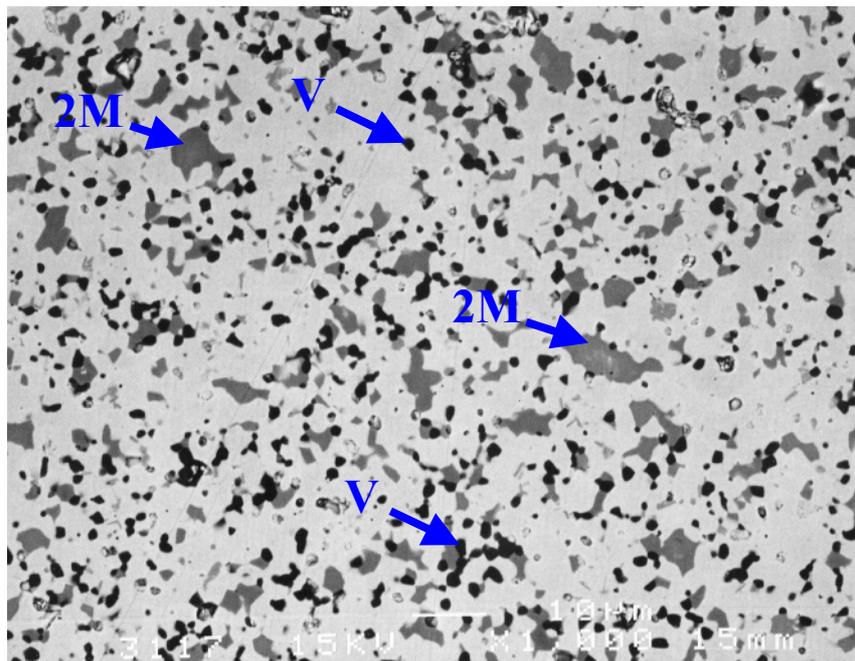


(b) — 10  $\mu\text{m}$ .

Figure I-17: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980358 (Pu103-01A) (Task 1.2, composition B1-15 (~10 % (nominal) phosphate), oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the lighter grey phase is Pu/U-brannerite, the grey phase is rutile (R) and the dark-grey phase is whitlockite (W). Porosity (A) and PuO<sub>2</sub> (O) are also present.



(a)



(b) — 10 μm.

Figure J-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980297 (Task 1.2, composition B1-2, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in 3.7% H<sub>2</sub>/Ar for 4 hours). The matrix is pyrochlore. 2M zirconolite (2M), perovskite (V, dark-grey) and porosity (A) are present.

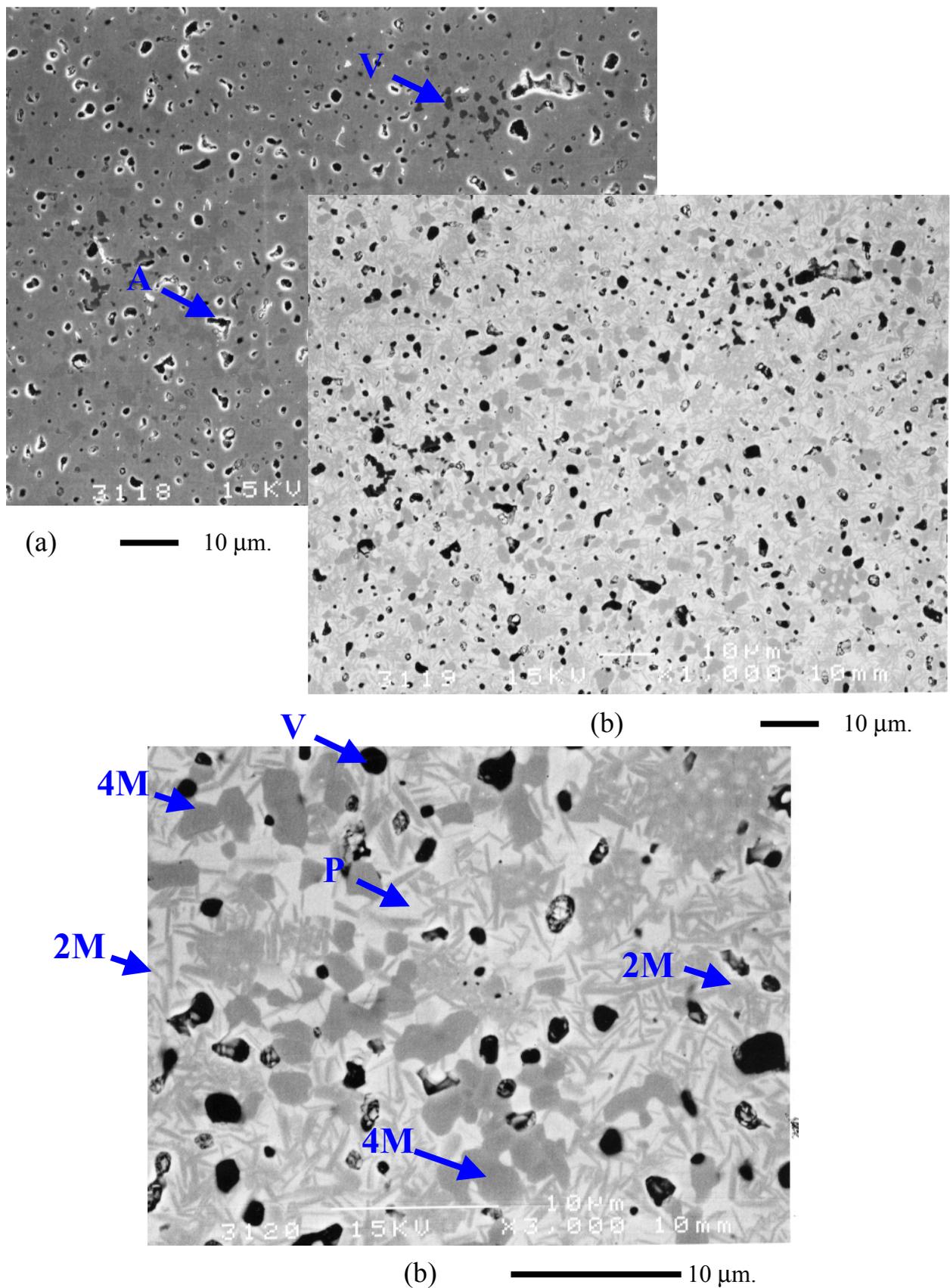


Figure J-2: (a) Secondary electron micrograph and, (b) and (c) backscattered electron micrographs of mws980299 (Task 1.2, composition B1-10, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in 3.7% H<sub>2</sub>/Ar for 4 hours). The matrix is a mixture of pyrochlore (P, light grey), 2M zirconolite (2M) and 4M zirconolite (4M). Perovskite (V, dark-grey) and porosity (A) are also present.

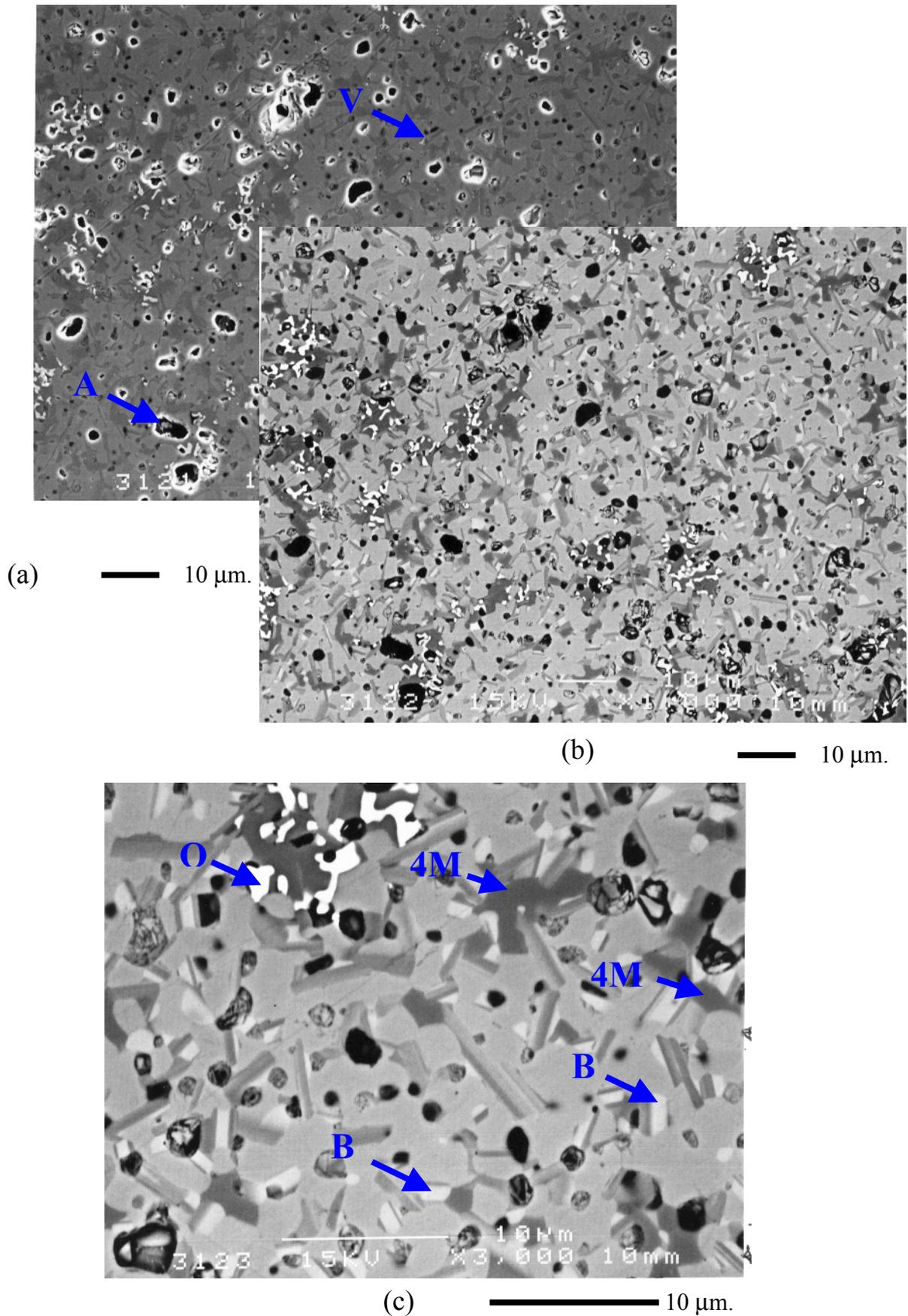


Figure J-3: (a) Secondary electron micrograph and, (b) and (c) backscattered electron micrographs of mws980301 (Task 1.2, composition B1-12, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in 3.7% H<sub>2</sub>/Ar for 4 hours). The matrix is pyrochlore (P, light grey). There is also what is believed to be 4M zirconolite (4M), Th/U-brannerite (B), which exhibits substantial zoning. (Th,U)O<sub>2</sub> (O) and porosity (A) are also present.



## **APPENDIX B**

### **X-RAY DIFFRACTION RESULTS OF THE SAMPLES FROM TASK 1.2**

## **B. APPENDIX B X-RAY DIFFRACTION RESULTS OF THE SAMPLES FROM TASK 1.2**

The following Table (B-1) contains a list of the raw data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The patterns are from polished surfaces of pellets. The broad low angle peak  $\sim 20 - 25^\circ$  (2 theta) in the patterns is from the resin used to mount the samples.

The raw data files are on the enclosed computer CD-ROM disk.

s\*.raw files are siemens D500 files

t\*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0

t\*.txt are text files of Scintag files

t\*.rd are Scintag files exported as older version Scintag binary files.

**Table B-1 Raw x-ray diffraction data file names for the samples of Task 1.2.**

Batch Description	Milling Time (h)	Sint. Temp. (°C)	Sint. Time (h)	Sint. atm.*	Sample No.	Raw Data File Names
<i>Th/U-doped Batches</i>						
<i>Baseline</i>						
B1-2 Alkoxide wet	4	1350	4	Ar	mws980106	s14428
B1-2 Alkoxide wet	16	1350	4	Ar	mws980173	s14567
B1-2 Alkoxide wet	16	1300	4	Ar	mws980309	s14721
B1-2 Alkoxide wet	16	1400	4	Ar	mws980323	s14729 <sup>§</sup>
B1-2 Alkoxide wet	16	1350	75	Ar	mws980348	s14890
B1-2 Alkoxide wet	16	1350	4	3.7% H <sub>2</sub>	mws980297	s14674
B1-2 Oxide dry	4	1350	4	Ar	mws980134	s14448
B1-2 Oxide dry	16	1350	4	Ar	mws980139	s14450
B1-2 Oxide wet	4	1350	4	Ar	mws980133	s14447
B1-2 Oxide wet	16	1350	4	Ar	mws980137	s14449
B1-2 Oxide wet	16	1400	4	Ar	mws980407	
B1-2 Oxide wet	16	1350	75	Ar	mws980391	s14947
<i>Baseline + impurities</i>						
B1-4 Alkoxide wet	4	1350	4	Ar	mws980112	s14446
B1-4 Alkoxide wet	16	1350	4	Ar	mws980177	s14569
B1-4 Alkoxide wet	16	1300	4	Ar	mws980317	s14725 <sup>§</sup>
B1-4 Alkoxide wet	16	1400	4	Ar	mws980303	s14718
B1-4 Alkoxide wet	16	1350	75	Ar	mws980351	s14893
B1-4 Oxide dry	16	1350	4	Ar	mws980151	s14455
B1-4 Oxide wet						
B1-4 Oxide wet	16	1350	4	Ar	mws980149	s14452
B1-4 Oxide wet	16	1400	4	Ar	mws980408	
B1-4 Oxide wet	16	1350	75	Ar	mws980394	s14979
<i>Zirconolite-rich</i>						
B1-10 Alkoxide wet	4	1350	4	Ar	mws980108	s14528
B1-10 Alkoxide wet	16	1350	4	Ar	mws980175	s14568
B1-10 Alkoxide wet	16	1300	4	Ar	mws980311	s14722
B1-10 Alkoxide wet	16	1400	4	Ar	mws980325	s14728 <sup>§</sup>
B1-10 Alkoxide wet	16	1350	75	Ar	mws980349	s14891
B1-10 Alkoxide wet	16	1350	4	3.7% H <sub>2</sub>	mws980299	s14675
B1-10 Oxide dry	16	1350	4	Ar	mws980147	s14451
B1-10 Oxide wet	16	1350	4	Ar	mws980145	s14458
B1-10 Oxide wet	16	1400	4	Ar	mws980409	
B1-10 Oxide wet	16	1350	75	Ar	mws980395	s14980
<i>Brannerite-rich</i>						
B1-12 Alkoxide wet	4	1350	4	Ar	mws980110	s14529
B1-12 Alkoxide wet	16	1350	4	Ar	mws980179	s14570
B1-12 Alkoxide wet	16	1300	4	Ar	mws980313	s14723
B1-12 Alkoxide wet	16	1400	4	Ar	mws980326	s14730
B1-12 Alkoxide wet	16	1350	75	Ar	mws980350	s14892
B1-2 Alkoxide wet	16	1350	4	3.7% H <sub>2</sub>	mws980301	s14676
B1-12 Oxide dry	16	1350	4	Ar	mws980143	s14457
B1-12 Oxide wet	16	1350	4	Ar	mws980141	s14456
B1-12 Oxide wet	16	1400	4	Ar	mws980410	
B1-12 Oxide wet	16	1350	75	Ar	mws980396	s14981
<i>Nominally 10 % perovskite</i>						
B1-14 Alkoxide wet	16	1350	4	Ar	mws980262	s14677
B1-14 Alkoxide wet	16	1350	4	air	mws980268	s14678
B1-14 Alkoxide wet	16	1300	4	Ar	mws980319	s14724 <sup>§</sup>
B1-14 Alkoxide wet	16	1400	4	Ar	mws980305	s14719
B1-14 Alkoxide wet	16	1350	75	Ar	mws980392	s14948

B1-14 Oxide dry	16	1350	4	Ar	mws980283	s14680
B1-14 Oxide dry	16	1350	4	air	mws980288	s14682
B1-14 Oxide wet	16	1350	4	Ar	mws980282	s14679
B1-14 Oxide wet	16	1350	4	air	mws980286	s14681
B1-14 Oxide wet	16	1400	4	Ar	mws980411	
B1-14 Oxide wet	16	1350	75	Ar	mws980397	s14982
<i>~ 10 % phosphate</i>						
B1-16 Alkoxide wet	16	1350	4	Ar	mws980274	s14670
B1-16 Alkoxide wet	16	1350	4	air	mws980280	s14673
B1-16 Alkoxide wet	16	1300	4	Ar	mws980321	s14726
B1-16 Alkoxide wet	16	1400	4	Ar	mws980307	s14720
B1-16 Alkoxide wet	16	1350	75	Ar	mws980392	s14949
B1-16 Oxide dry	16	1350	4	Ar	mws980272	s14669
B1-16 Oxide dry	16	1350	4	air	mws980278	s14672 – poor pattern
B1-16 Oxide wet	16	1350	4	Ar	mws980270	s14668
B1-16 Oxide wet	16	1350	4	air	mws980276	s14671
B1-16 Oxide wet	16	1400	4	Ar	mws980412	
B1-16 Oxide wet	16	1350	75	Ar	mws980398	s14983
<b><i>Pu/U-doped</i></b>						
<i>Baseline</i>						
B1-1 Alkoxide wet	16	1350	4	Ar	Pu092-01	t1247
B1-1 Oxide dry	16	1350	4	Ar	Pu67-1350	t509
B1-1 Oxide wet	16	1350	4	Ar	Pu68	t1241
<i>Baseline + impurities</i>						
B1-3 (A-9) Alkoxide wet	16	1350	4	Ar	Pu73	t495
A-7 Oxide wet	16	1350	4	Ar	Pu75	s14880
<i>Zirconolite-rich</i>						
B1-9 Alkoxide wet	16	1350	4	Ar	Pu093-01	t1243
B1-9 Oxide dry	16	1350	4	Ar	Pu098-01	s15049
B1-9 Oxide wet	16	1350	4	Ar	Pu097-01	s15048
<i>Brannerite-rich</i>						
B1-11 Alkoxide wet	16	1350	4	Ar	Pu094-01	t1244
B1-11 Oxide dry	16	1350	4	Ar	Pu100-01	s15051
B1-11 Oxide wet	16	1350	4	Ar	Pu099-01	s15050
<i>Nominally 10 % perovskite</i>						
B1-13 Alkoxide wet	16	1350	4	Ar	Pu105-01	s15054, t1339
B1-13 Oxide dry	16	1350	4	Ar	Pu102-01	s15067
B1-13 Oxide wet	16	1350	4	Ar	Pu101-01	s15052
<i>~ 10 % phosphate</i>						
B1-15 Alkoxide wet	16	1350	4	Ar	Pu106-01	t1347
B1-15 Oxide dry	16	1350	4	Ar	Pu104-01	t1341
B1-15 Oxide wet	16	1350	4	Ar	Pu103-01	t1340

\* 3.7 % H<sub>2</sub> = 3.7 % H<sub>2</sub> in argon

## **APPENDIX C**

**SCANNING ELECTRON MICROGRAPHS AND  
ENERGY DISPERSIVE X-RAY SPECTROMETRY  
RESULTS FOR SAMPLES OF COMPOSITION B1-2 -  
Th/U-DOPED BASELINE CERAMIC**

## C. APPENDIX C: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-2 - Th/U-DOPED BASELINE CERAMIC

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M zirc	2M zirconolite
4M zirc	4M zirconolite
Rutile	rutile (Hf-doped)
Whit	whitlockite

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table C-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped alkoxide-route batches, which were wet-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980106					mws980173		
	Wet-mill 4 h					Wet-mill 16 h		
	Pyr dense region	Pyr porous region	Bran dense region	Bran porous region	Rutile	Pyr	Bran	Rutile
~ abundance (vol. %)	75 - 85		10 - 20		5	80 - 85	10 - 15	5
Element								
oxygen	7	7	6	6	2	7	6	2
Ca	0.93	0.92	0.09	0.06	0.007	0.89	0.06	0.005
Gd	0.19	0.20	0.11	0.12		0.19	0.09	
Hf	0.26	0.25	0.15	0.13	0.07	0.24	0.13	0.06
U	0.44	0.43	0.37	0.37	0.006	0.42	0.40	0.005
Th	0.19	0.18	0.38	0.38	0.002	0.20	0.36	0.001
Ti	2.01	2.03	1.98	1.99	0.92	2.05	2.00	0.93
<b>Total</b>	4.01	4.01	3.07	3.06	1.00	3.99	3.06	1.00

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table C-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped oxide-route batches, which were dry-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours. Note that the 4 hour dry-milled sample (mws980134) is inhomogeneous and the values for composition are given as a guide.**

Sample No.	mws980134					mws980139				
	Dry-mill 4 h					Dry-mill 16 h				
	Pyr	2M Zirc	Bran	Rutile	Oxide	Pyr	4M Zirc	Bran	Rutile	Oxide
~ abundance (vol. %)	45 - 60	10 - 20	20 - 25	5	5	55 - 65	5 - 10	20 - 25	5	5
Element										
oxygen	7	7	6	2	2	7	7	6	2	2
Ca	1.02	0.92	0.05	0.002		1.07	0.96	0.08	0.003	
Gd	0.24	0.14	0.11			0.24	0.23	0.13		
Hf	0.25	0.86	0.13	0.04		0.19	0.50	0.11	0.07	
U	0.43	0.08	0.38	0.002		0.53	0.29	0.43	0.003	0.003
Th	0.13	0.01	0.39		1.00	0.09	0.08	0.32		0.997
Ti	2.00	1.99	1.99	0.96		1.99	1.98	2.00	0.93	
<b>Total</b>	4.07	4.00	3.05	1.00	1.00	4.10	4.04	3.07	1.01	1.00

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table C-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped oxide-route batches, which were wet-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980133						mws980137				
	Wet-mill 4 h						Wet-mill 16 h				
	Pyr	4M Zirc	Bran	Rutile	Oxide	Whit	Pyr	4M Zirc	Bran	Rutile	Oxide
~ abundance (vol. %)	55 - 60	5 - 10	25	5	5	<< 1	65 - 70	5	20 - 25	3	1
Element											
oxygen	7	7	6	2	2	8	7	7	6	2	2
Ca	0.99	0.95	0.05	0.003		2.64	1.03	0.99	0.09	0.009	0.005
Gd	0.27	0.22	0.13	0.003		0.17	0.24	0.22	0.14		
Hf	0.27	0.47	0.15	0.08			0.25	0.42	0.13	0.07	
U	0.41	0.29	0.39	0.002		0.008	0.41	0.31	0.43	0.005	0.09
Th	0.14	0.08	0.35		0.998	0.03	0.15	0.09	0.31	0.001	0.87
Ti	1.98	2.03	1.99	0.92	0.002		1.99	2.02	1.99	0.92	0.04
P <sup>#</sup>						2.01					
<b>Total</b>	4.07	4.03	3.06	1.00	1.00	4.86	4.08	4.05	3.08	1.01	1.00

# P is from anatase raw material

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table C-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped alkoxide-route batches, which were sintered in Ar at 1300 for 4 hours, 1400°C for 4 hours and 1375°C for 75 hours.**

<b>Sample No.</b>	<b>mws980309</b>				<b>mws980323</b>			<b>mws980348</b>		
	<b>1300°C 4 h</b>				<b>1400°C 4 h</b>			<b>1350°C 75 h</b>		
	<b>Pyr</b>	<b>4M Zirc</b>	<b>Bran</b>	<b>Rutile</b>	<b>Pyr</b>	<b>Bran</b>	<b>Rutile</b>	<b>Pyr</b>	<b>Bran</b>	<b>Rutile</b>
<b>~ abundance (vol. %)</b>	<b>70 - 80</b>	<b>2 - 3</b>	<b>15 - 20</b>	<b>5</b>	<b>80 - 90</b>	<b>10 - 15</b>	<b>2</b>	<b>80 - 90</b>	<b>10 - 15</b>	<b>3</b>
<b>Element</b>										
<b>oxygen</b>	<b>7</b>	<b>7</b>	<b>6</b>	<b>2</b>	<b>7</b>	<b>6</b>	<b>2</b>	<b>7</b>	<b>6</b>	<b>2</b>
<b>Ca</b>	0.91	0.84	0.06	0.02	0.88	0.06	0.001	0.91	0.05	0.002
<b>Gd</b>	0.20	0.18	0.08		0.20	0.08	0.002	0.23	0.10	
<b>Hf</b>	0.25	0.45	0.12	0.06	0.24	0.13	0.07	0.21	0.11	0.06
<b>U</b>	0.43	0.32	0.38	0.02	0.43	0.40	0.005	0.43	0.43	0.006
<b>Th</b>	0.19	0.13	0.45	0.006	0.19	0.36	0.001	0.19	0.36	0.001
<b>Ti</b>	2.03	2.04	1.97	0.90	2.06	2.01	0.93	2.04	2.00	0.94
<b>Total</b>	4.00	3.96	3.05	1.01	4.00	3.05	1.00	4.01	3.05	1.00

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system.

**Table C-5: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped wet-milled oxide-route batches, which were sintered in Ar at 1400°C for 4 hours and at 1350°C for 75 hours.**

<b>Sample No.</b>	<b>mws980407</b>			<b>mws980391</b>		
	<b>1400°C 4 h</b>			<b>1350°C 75 h</b>		
	<b>Pyr</b>	<b>Bran</b>	<b>Oxide</b>	<b>Pyr</b>	<b>Bran</b>	<b>Whit</b>
<b>~ abundance (vol. %)</b>	<b>80 - 85</b>	<b>15 - 20</b>	<b>&lt; 1</b>	<b>85</b>	<b>15</b>	<b>&lt; 1</b>
<b>Element</b>						
<b>oxygen</b>	<b>7</b>	<b>6</b>	<b>2</b>	<b>7</b>	<b>6</b>	<b>8</b>
<b>Ca</b>	0.99	0.05	0.01	0.93	0.05	2.58
<b>Gd</b>	0.24	0.12	0.03	0.21	0.09	0.16
<b>Hf</b>	0.24	0.13	0.008	0.28	0.16	
<b>U</b>	0.42	0.39	0.11	0.41	0.44	0.003
<b>Th</b>	0.17	0.38	0.70	0.18	0.33	0.01
<b>Ti</b>	2.00	1.99	0.15	2.02	1.96	0.007
<b>P<sup>#</sup></b>						2.00
<b>Total</b>	4.06	3.06	1.01	4.02	3.05	4.90

# P is from anatase raw material

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system.

## **APPENDIX D**

**SCANNING ELECTRON MICROGRAPHS AND ENERGY  
DISPERSIVE X-RAY SPECTROMETRY RESULTS FOR  
SAMPLES OF COMPOSITION B1-4 - Th/U-DOPED  
BASELINE + IMPURITIES CERAMIC**

## D. APPENDIX D: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-4 - Th/U-DOPED BASELINE + IMPURITIES CERAMIC

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)
Silicate	alumino-silicate phase, probably a glass

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table D-1: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from the Task 1.2, B1-4, Th/U-doped alkoxide-route batches, which were wet-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980112				mws980177			
	Wet-mill 4 h				Wet-mill 16 h			
	Pyr	2M Zirc	Bran	Silicate <sup>\$</sup>	Pyr	2M Zirc	Bran	Silicate <sup>\$</sup>
~ abundance (vol. %)	70 - 80	7 - 10	15	1 - 2	80 - 85	7 - 10	7 - 10	1
Element	Wt. %				Wt. %			
oxygen	7	7	6	42	7	7	6	43
Ca	0.91	0.68	0.07	7.3	0.89	0.71	0.04	6.6
Gd	0.19	0.17	0.13	0.8	0.23	0.18	0.11	0.6
Hf	0.24	0.79	0.13		0.18	0.65	0.10	1.8
U	0.45	0.17	0.40	1.7	0.44	0.15	0.44	2.6
Th	0.21	0.08	0.37	0.7	0.19	0.07	0.37	1.3
Ti	1.98	1.72	1.95	7.4	1.96	1.91	1.96	8.9
Mg	0.04	0.05		0.7	0.09	0.05		1.5
Al		0.23	0.04	7.3		0.12	0.04	16.5
Ga		0.12		8.1		0.16		9.4
K				0.7				0.6
Na				3.6				1.3
Si				19.9				45.3
Ta					0.03			
W					0.005			
B								
Cr								
Zn								
<b>Total</b>	4.02	3.99	3.07	100	4.05	3.99	3.06	100

<sup>\$</sup> typical values

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table D-2: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from the Task 1.2, B1-4, Th/U-doped oxide-route batches, which were dry-milled or wet-milled 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980151				mws980149			
	Dry-mill				Wet-mill			
	Pyr	2M Zirc	Bran	Silicate <sup>\$</sup>	Pyr	2M Zirc	Bran	Silicate <sup>\$</sup>
~ abundance (vol. %)	78 - 79	10	10	1 - 2	78 - 79	10	10	1 - 2
Element	Wt. %				Wt. %			
oxygen	7	7	6	42	7	7	6	41
Ca	0.99	0.75	0.05		0.99	0.75	0.03	14
Gd	0.25	0.20	0.12		0.26	0.20	0.08	1.6
Hf	0.16	0.65	0.10		0.17	0.65	0.06	1.1
U	0.44	0.15	0.41		0.44	0.17	0.24	1.9
Th	0.17	0.06	0.38		0.18	0.06	0.67	1.1
Ti	1.97	1.87	1.95		1.95	1.85	1.93	6.1
Mg	0.06	0.06			0.05	0.06		62.2
Al	0.01	0.15	0.06		0.02	0.14	0.03	6.8
Ga		0.14				0.14		5.4
K								
Na								
Si								14.1
Ta	0.02				0.02			
W	0.006				0.01			
Mo								0.7
Fe								0.2
P								3.4
B								
Cr								
Zn								
<b>Total</b>	4.08	4.03	3.07	100	4.07	4.02	3.04	100

<sup>\$</sup> typical values

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table D-3: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from the Task 1.2, B1-4, Th/U-doped alkoxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1300°C for 4 hours, 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980317					mws980303				mws980351			
	1300°C 4 h					1400°C 4 h				1375°C 75 h			
	Pyr	2M Zirc	Bran	Oxide <sup>&amp;</sup>	Silicate <sup>§, &amp;</sup>	Pyr	2M Zirc	Bran	Silicate <sup>§</sup>	Pyr	2M Zirc	Bran	Silicate <sup>§</sup>
~ abundance (vol. %)	70 - 75	10 - 15	15	<< 1	1 - 2	70 - 80	10 - 15	10	1 - 2	70 - 80	10 - 15	10	1 - 2
<b>Element</b>	<b>Wt. %</b>					<b>Wt. %</b>				<b>Wt. %</b>			
<b>oxygen</b>	7	7	6			7	7	6	41	7	7	6	41
<b>Ca</b>	0.95	0.73	0.07			0.87	0.66	0.07	7	0.90	0.72	0.04	12
<b>Gd</b>	0.22	0.9	0.13			0.20	0.15	0.10	0.7	0.22	0.17	0.10	
<b>Hf</b>	0.15	0.65	0.09			0.26	0.80	0.12	0.9	0.18	0.66	0.10	
<b>U</b>	0.45	0.17	0.40			0.44	0.15	0.42	3	0.44	0.14	0.44	0.4
<b>Th</b>	0.19	0.07	0.38			0.20	0.07	0.37	1.5	0.20	0.07	0.37	0.4
<b>Ti</b>	1.98	1.86	1.99			1.93	1.75	1.97	6.6	1.98	1.92	1.95	4.8
<b>Mg</b>	0.07	0.07				0.02	0.07		1	0.06	0.07		1.7
<b>Al</b>	0.01	0.14	0.03			0.05	0.17	0.02	8.5	0.02	0.15	0.06	9
<b>Ga</b>		0.15					0.16		7.5		0.11		4.6
<b>K</b>									0.5				0.04
<b>Na</b>									3				1.6
<b>Si</b>									18				22
<b>Ta</b>	0.02					0.03				0.03			
<b>W</b>	0.007									0.006			
<b>Mo</b>													
<b>Ni</b>													0.3
<b>Fe</b>									0.1				0.4
<b>P</b>													
<b>B</b>													
<b>Cr</b>													
<b>Zn</b>													
<b>Total</b>	4.07	4.02	3.08			4.00	3.99	3.07	100	4.03	3.06	4.01	100

§ typical values

& too small a grain size to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table D-4: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from the Task 1.2, B1-4, Th/U-doped oxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980408						mws980394				
	1400°C 4 h						1350°C 75 h				
	Pyr	Pyr – Zirc? “late stage”*	2M Zirc	Bran	Oxide	Silicate <sup>§</sup>	Pyr	2M Zirc	Bran	Oxide in bran grain`	Silicate <sup>§</sup>
~ abundance (vol. %)	70 - 80	1	10 - 15	10	< 1	1 - 2	70 - 80	10 - 15	10	< 1	1 - 2
Element	Wt. %						Wt. %				
oxygen	7		7	6	2	42	7	7	6	2	43
Ca	0.94	0.66	0.73	0.04		15	0.93	0.73	0.04		16
Gd	0.24	0.19	0.19	0.11	0.04	0.6	0.24	0.19	0.08		0.9
Hf	0.20	0.29	0.66	0.11	0.006	0.4	0.17	0.68	0.09		0.4
U	0.44	0.12	0.16	0.44	0.11	1.1	0.44	0.14	0.41	0.08	0.1
Th	0.19	0.07	0.06	0.36	0.81	0.6	0.19	0.06	0.44	0.86	0.3
Ti	1.93	2.26	1.87	1.96	0.04	5	1.98	1.87	1.95	0.07	5
Mg	0.08	0.07	0.05			1.8		0.08			1.6
Al	0.02	0.18	0.16	0.04		8	0.03	0.16	0.05		8
Ga		0.17	0.13			5		0.10			3
K						0.07					
Na											0.04
Si						15					18
Ta	0.03	0.03					0.02				
W	0.004						0.02				
Mo						0.7					
Fe						0.4					0.4
P						3					3
B											
Cr											
Zn											
<b>Total</b>	4.06	3.99	4.01	3.06	1.01	100	4.02	4.02	3.05	1.00	100

§ Typical values

\* “Late stage” pyrochlore or zirconolite, which is associated with the glass

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX E**

**SCANNING ELECTRON MICROGRAPHS AND  
ENERGY DISPERSIVE X-RAY SPECTROMETRY  
RESULTS FOR SAMPLES OF COMPOSITION B1-10 -  
Th/U-DOPED ZIRCONOLITE-RICH CERAMIC**

## E. APPENDIX E: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-10 - Th/U-DOPED ZIRCONOLITE-RICH CERAMIC

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table E-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-10, Th/U-doped alkoxide-route batches, which were wet-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980108			mws980175		
	Wet-mill 4 h			Wet-mill 16 h		
	Pyr	2M Zirc	Bran	Pyr	2M Zirc	Bran
~ abundance (vol. %)	45 - 55	30 - 40	15	50 - 55	35 - 40	15
<b>Element</b>						
<b>oxygen</b>	7	7	6	7	7	6
<b>Ca</b>	0.99	0.84	0.08	0.97	0.82	0.11
<b>Gd</b>	0.20	0.15	0.12	0.20	0.12	0.10
<b>Hf</b>	0.34	0.81	0.17	0.30	0.82	0.17
<b>U</b>	0.38	0.11	0.38	0.39	0.09	0.39
<b>Th</b>	0.18	0.04	0.34	0.19	0.04	0.36
<b>Ti</b>	1.92	1.84	1.92	1.99	1.87	1.95
<b>Al</b>	0.05	0.21	0.05		0.24	
<b>Total</b>	4.06	4.01	3.08	4.02	4.00	3.08

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table E-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-10, Th/U-doped oxide-route batches, which were dry-milled or wet-milled 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980147						mws980145				
	Dry-mill						Wet-mill				
	Pyr	2M Zirc	Bran	Oxide ThO <sub>2</sub>	Rutile	Oxide UO <sub>2</sub>	Pyr	2M Zirc	Bran	Oxide ThO <sub>2</sub> &	Oxide UO <sub>2</sub>
~ abundance (vol. %)	35 - 40	30	20	5 - 10	3	1 - 2	40 - 50	30 - 40	20	< 1	< 1
<b>Element</b>											
<b>oxygen</b>	7	7	6	2	2	2	7	7	6	2	2
<b>Ca</b>	1.01	0.84	0.06			0.17	0.99	0.83	0.03		0.04
<b>Gd</b>	0.26	0.14	0.12			0.02	0.29	0.17	0.07		0.03
<b>Hf</b>	0.24	0.88	0.12	0.001	0.05	0.01	0.26	0.075	0.13		0.01
<b>U</b>	0.46	0.06	0.42	0.01	0.005	0.88	0.40	0.10	0.41		0.87
<b>Th</b>	0.11	0.04	0.33	0.99		0.008	0.18	0.04	0.41		0.03
<b>Ti</b>	1.98	1.84	1.98		0.95	0.001	1.96	1.92	1.98		0.05
<b>Al</b>		0.22	0.04					0.20	0.02		
<b>Total</b>	4.07	4.01	3.07	1.00	1.00	1.09	4.07	4.01	3.04		1.03

& Too small to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table E-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-10, Th/U-doped alkoxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1300°C for 4 hours, 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980311			mws980325			mws980349		
	1300°C 4 h			1400°C 4 h			1375°C 75 h		
	Pyr	2M Zirc	Bran	Pyr	2M Zirc	Bran	Pyr	2M Zirc	Bran
~ abundance (vol. %)	30 - 50	30 - 40	20 - 30	40	40	20	40	40	20
<b>Element</b>									
<b>oxygen</b>	7	7	6	7	7	6	7	7	6
<b>Ca</b>	0.98	0.83	0.05	0.95	0.81	0.04	0.97	0.86	0.03
<b>Gd</b>	0.20	0.13	0.08	0.22	0.13	0.08	0.23	0.17	0.08
<b>Hf</b>	0.29	0.83	0.15	0.31	0.83	0.16	0.26	0.70	0.13
<b>U</b>	0.41	0.12	0.31	0.39	0.09	0.33	0.39	0.15	0.36
<b>Th</b>	0.20	0.04	0.50	0.19	0.03	0.46	0.20	0.06	0.46
<b>Ti</b>	1.95	1.84	1.93	1.97	1.88	1.97	1.98	1.91	1.95
<b>Al</b>	0.01	0.21	0.01		0.23		0.02	0.18	0.03
<b>Total</b>	4.04	4.00	3.05	4.03	4.00	3.04	4.05	4.02	

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table E-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-10, Th/U-doped oxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980409				mws980395			
	1400°C 4 h				1350°C 75 h			
	Pyr	2M Zirc	Bran	Oxide	Pyr	2M Zirc	Bran	Oxide
~ abundance (vol. %)	30 – 40	40	20 – 30	<< 1	40	40	20	<< 1
<b>Element</b>								
<b>oxygen</b>	7	7	6	2	7	7	6	2
<b>Ca</b>	0.96	0.83	0.02	0.04	0.96	0.82	0.03	0.06
<b>Gd</b>	0.25	0.15	0.08	0.04	0.03	0.16	0.09	0.03
<b>Hf</b>	0.29	0.79	0.13	0.007	0.27	0.79	0.13	0.008
<b>U</b>	0.40	0.10	0.25	0.19	0.40	0.09	0.39	0.75
<b>Th</b>	0.20	0.04	0.59	0.69	0.20	0.04	0.45	0.04
<b>Ti</b>	1.95	1.89	1.94	0.06	1.96	1.89	1.93	0.14
<b>Al</b>		0.22	0.02			0.22	0.03	
<b>Total</b>	4.05	4.01	3.03	1.03	4.04	4.01	3.04	1.04

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX F**

**SCANNING ELECTRON MICROGRAPHS AND  
ENERGY DISPERSIVE X-RAY SPECTROMETRY  
RESULTS FOR SAMPLES OF COMPOSITION B1-12 -  
Th/U-DOPED BRANNERITE-RICH CERAMIC**

## F. APPENDIX F: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-12 - Th/U-DOPED BRANNERITE-RICH CERAMIC

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table F-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-12, Th/U-doped alkoxide-route batches, which were wet-milled for 4 or 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980110			mws980179	
	Wet-mill 4 h			Wet-mill 16 h	
	Pyr	Bran	Rutile &	Pyr	Bran
~ abundance (vol. %)	50 – 60	40 - 50	< 1	50 – 60	40 - 50
<b>Element</b>					
<b>oxygen</b>	7	6		7	6
<b>Ca</b>	1.04	0.09		0.99	0.09
<b>Gd</b>	0.20	0.10		0.20	0.10
<b>Hf</b>	0.31	0.17		0.31	0.17
<b>U</b>	0.45	0.45		0.44	0.46
<b>Th</b>	0.12	0.27		0.13	0.27
<b>Ti</b>	1.95	1.99		1.98	1.98
<b>Total</b>	4.07	3.07		4.04	3.07

& Too small to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table F-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-12, Th/U-doped oxide-route batches, which were dry-milled or wet-milled 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980143						mws980141				
Sample No.	Dry-mill						Wet-mill				
	Pyr	2M Zirc	Bran	Rutile	Oxide ThO <sub>2</sub>	Oxide UO <sub>2</sub>	Pyr	2M Zirc	Bran	Rutile	Oxide
~ abundance (vol. %)	30 - 45	10	30-40	7	7 - 10	1	55 - 65	2 - 5	30 - 40	3 - 5	< 1
Element											
oxygen	7	7	6	2	2	2	7	7	6	2	2
Ca	0.94	0.87	0.02			0.05	0.97	0.80	0.05		0.07
Gd	0.31	0.13	0.07			0.07	0.28	0.13	0.12		0.06
Hf	0.22	0.82	0.11	0.07		0.01	0.27	0.88	0.14	0.08	0.01
U	0.48	0.08	0.37	0.004	0.006	0.88	0.42	0.07	0.49	0.005	0.83
Th	0.09	0.02	0.48	0.001	0.99	0.02	0.13	0.02	0.27		0.04
Ti	2.01	2.00	1.97	0.93		0.01	1.99	1.91	1.99	0.91	0.03
Al #		0.07						0.16			
<b>Total</b>	4.05	3.98	3.02	1.00	1.00	1.04	4.05	3.97	3.06	1.05	1.04

# Processing impurity

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table F-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-12, Th/U-doped alkoxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1300°C for 4 hours, 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980313			mws980326		mws980350		
	1300°C 4 h			1400°C 4 h		1375°C 75 h		
	Pyr	4M Zirc	Bran	Bran		Pyr	Bran	Rutile
~ abundance (vol. %)	55 - 58	2 - 3	40	50	50	45 - 50	45 - 50	2 - 3
<b>Element</b>								
<b>oxygen</b>	7	7	6	7	6	7	6	2
<b>Ca</b>	0.99	0.99	0.09	0.98	0.70	0.99	0.07	0.002
<b>Gd</b>	0.19	0.15	0.11	0.19	0.11	0.23	0.11	
<b>Hf</b>	0.31	0.51	0.16	0.31	0.17	0.26	0.14	0.08
<b>U</b>	0.45	0.33	0.45	0.44	0.45	0.14	0.28	0.005
<b>Th</b>	0.13	0.07	0.27	0.14	0.27	0.44	0.48	
<b>Ti</b>	1.96	2.01	1.99	1.97	1.99	1.99	1.98	0.92
<b>Total</b>	4.05	4.03	3.07	4.04	3.07	4.05	3.06	1.01

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table F-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-12, Th/U-doped oxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980410				mws980396		
	1400°C 4 h				1350°C 75 h		
	Pyr	Bran	Rutile	Oxide <sup>&amp;</sup>	Pyr	Bran	Rutile
~ abundance (vol. %)	45 – 50	45 – 50	1 -2	< 1	45 - 55	45 - 55	2 - 3
<b>Element</b>							
oxygen	7	6	2		7	6	2
Ca	0.95	0.05			0.98	0.03	
Gd	0.24	0.12			0.25	0.09	
Hf	0.27	0.14	0.08		0.25	0.13	0.08
U	0.44	0.47	0.007		0.44	0.50	0.005
Th	0.14	0.28			0.14	0.30	0.001
Ti	2.00	2.00	0.91		2.00	1.96	0.92
Al <sup>#</sup>						0.03	
<b>Total</b>	4.03	3.06	1.00		4.05	3.05	1.00

# Processing impurity

& Too small to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX G**

**SCANNING ELECTRON MICROGRAPHS AND  
ENERGY DISPERSIVE X-RAY SPECTROMETRY  
RESULTS FOR SAMPLES OF COMPOSITION B1-14 -  
Th/U-DOPED, NOMINALLY ~ 10 % PEROVSKITE  
CERAMIC**

## G. APPENDIX G: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-14 - Th/U-DOPED NOMINALLY ~ 10 % PEROVSKITE CERAMIC COMPOSITION

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)
Per	perovskite
Whit	whitlockite

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table G-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-14, Th/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980262				mws980283 <sup>+</sup>							mws980258		
	alkoxide				Dry-milled oxide							wet-milled oxide		
	Pyr	Bran	Oxide ThO <sub>2</sub>	Rutile &	Pyr	Bran	2M Zirc	Per	Oxide ThO <sub>2</sub> @	Oxide UO <sub>2</sub> @	Rutile <sup>v</sup>	Pyr	Rutile	Whit
~ abundance (vol. %)	93	5	1	1	66 - 71	5-10	20	7	5	1	1	93 - 95	5 - 7	<< 1
Element														
oxygen	7	6	2	2	7	6	7	4				7	2	8
Ca	0.98	0.06			0.85	0.14	0.90	0.83				0.90	0.003	2.63
Gd	0.19	0.07			0.18	0.03	0.09	0.03				0.19		0.13
Hf	0.26	0.13			0.23	0.10	0.88	0.01				0.25	0.06	
U	0.35	0.30			0.45	0.07	0.04	0.01				0.34	0.002	0.002
Th	0.22	0.51	1.00		0.20	0.83	0.03	0.04				0.23	0.001	0.01
Ti	2.03	1.97			2.06		2.03	1.00				2.08	0.94	0.02
P*														2.00
Mg#														0.11
<b>Total</b>	4.04	3.05	1.00		3.97	3.08	3.97	1.92				4.00	1.00	4.91

+ This sample is inhomogeneous; values here are given as a guide as the actual composition is variable across the pellet

\* From anatase raw material

# Processing impurity, source unknown

@ Composition of (Th,U)O<sub>2</sub> ranges from ThO<sub>2</sub> - UO<sub>2</sub>

& Grain size is too small to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table G-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-14, Th/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in air at 1350°C for 4 hours.**

Sample No.	mws980268				mws980288 <sup>+</sup>					mws980286			
	alkoxide				Dry-milled oxide					wet-milled oxide			
	Pyr	Bran	Oxide ThO <sub>2</sub> <sup>&amp;</sup>	Rutile <sup>&amp;</sup>	Pyr	Bran	4M Zirc	Rutile	Oxide ThO <sub>2</sub>	Pyr	Bran	Rutile	Oxide ThO <sub>2</sub> <sup>&amp;</sup>
~ abundance (vol. %)	92	7	1	<1	68 - 77	10	10 - 15	1 - 2	3 - 5	80	10	10	<1
<b>Element</b>													
<b>oxygen</b>	7	6			7	6	7	2	2	7	6	2	
<b>Ca</b>	1.06	0.08			1.05	0.09	0.91	0.004	0.004	1.07	0.09	0.005	
<b>Gd</b>	0.19	0.10			0.24	0.10	0.19		0.004	0.21	0.10		
<b>Hf</b>	0.27	0.15			0.15	0.14	0.47	0.06	0.003	0.25	0.14	0.10	
<b>U</b>	0.37	0.27			0.41	0.30	0.26	0.004	0.03	0.37	0.28	0.002	
<b>Th</b>	0.21	0.27			0.16	0.46	0.05	0.001	0.95	0.19	0.48	0.002	
<b>Ti</b>	1.97	1.98			1.98	1.98	2.12	0.94	0.02	1.99	1.98	0.89	
<b>Total</b>	4.08	3.06			4.09	3.07	4.08	1.01	1.01	4.08	3.07	1.00	

+ sample is inhomogeneous values here are given as a guide, the actual composition is variable across the pellet

& too small to measure

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table G-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-14, Th/U-doped alkoxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1300°C for 4 hours, 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980319					mws980305		mws980392	
	1300°C 4 h					1400°C 4 h		1375°C 75 h	
	Pyr	Bran high in Th	Bran	Oxide ThO <sub>2</sub>	Rutile	Pyr	Bran	Pyr	Bran
~ abundance (vol. %)	77 - 83	15 - 20		2 - 3	< 1	85	15	93 - 97	3 - 7
<b>Element</b>									
<b>oxygen</b>	7	6		2	2	7	6	7	6
<b>Ca</b>	0.99	0.05	0.05			0.97	0.06	0.94	0.05
<b>Gd</b>	0.19	0.06	0.06			0.20	0.09	0.20	0.09
<b>Hf</b>	0.27	0.12	0.13		0.07	0.27	0.14	0.26	0.15
<b>U</b>	0.36	0.19	0.28	0.05		0.37	0.31	0.36	0.37
<b>Th</b>	0.21	0.67	0.56	0.95		0.22	0.47	0.23	0.42
<b>Ti</b>	2.02	1.95	1.95		0.93	2.01	1.99	2.04	1.96
<b>Total</b>	4.04	3.04	3.03	1.00	1.00	4.03	3.06	4.03	3.05

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table G-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-14, Th/U-doped oxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980411			mws980397		
	1400°C 4 h			1350°C 75 h		
	Pyr	Bran	Rutile	Pyr	Bran	Rutile
~ abundance (vol. %)	85 - 88	5	7 - 10	88 - 90	5	5 - 7
<b>Element</b>						
<b>oxygen</b>	7	6	2	7	6	2
<b>Ca</b>	0.96	0.04		0.97	0.03	
<b>Gd</b>	0.23	0.09		0.23	0.09	
<b>Hf</b>	0.21	0.12	0.06	0.21	0.11	0.06
<b>U</b>	0.37	0.38	0.004	0.38	0.40	0.003
<b>Th</b>	0.21	0.42	0.001	0.22	0.42	0.001
<b>Ti</b>	2.06	1.98	0.94	2.04	1.99	0.94
<b>Total</b>	4.04	3.04	1.00	4.04	3.04	1.00

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX H**

**SCANNING ELECTRON MICROGRAPHS AND ENERGY  
DISPERSIVE X-RAY SPECTROMETRY RESULTS FOR  
SAMPLES OF COMPOSITION B1-16 - Th/U-DOPED,  
NOMINALLY ~ 10 % PHOSPHATE CERAMIC**

## H. APPENDIX H: SEM/EDS RESULTS FOR SAMPLES OF COMPOSITION B1-16 - Th/U-DOPED, NOMINALLY ~ 10 % PHOSPHATE CERAMIC

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)
Per	perovskite
Whit	whitlockite

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table H-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-16, Th/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	mws980274			mws980272 <sup>+</sup>							mws980270			
	alkoxide			Dry-milled oxide							wet-milled oxide			
	Pyr	Bran	Whit	Pyr	Bran	2M Zirc	Whit	Oxide <sup>@</sup>	Rutile	Hafnia	Pyr	Bran	Whit	Oxide <sup>*</sup>
~ abundance (vol. %)	70	20	10	51 -64	10	10 - 20	10	5 - 7	1 - 2	< 1	75	15	10	< 1
Element														
oxygen	7	6	8	7	6	7	8		2	2	7	2	8	
Ca	0.82	0.04	2.57	0.81	0.003-0.18	0.79	2.61		0.003	0.004	0.86	0.02	2.59	
Gd	0.24	0.04	0.17	0.25	0.04	0.12	0.20		0.001	0.001	0.19	0.04	0.16	
Hf	0.28	0.17	0.02	0.20-0.29	0.07-0.11	0.92			0.09	0.68	0.26	0.13		
U	0.39	0.42	0.04	0.38-0.58	0.25-0.81	0.06	0.003		0.002	0.006	0.43	0.36-0.44	0.02	
Th	0.22	0.42	0.04	0.11-0.19	0.09-0.65	0.03	0.01		0.001		0.24	0.44-0.54	0.02	
Ti	2.02	1.92	0.11	2.02	1.93-1.98	1.99	0.03		0.90	0.31	2.00	1.96	0.06	
P		0.01	1.83				2.00						1.98	
Si <sup>#</sup>			0.01											
<b>Total</b>	3.97	3.03	4.87	3.97	3.01	3.93	4.86		1.00	1.00	3.98	3.02	4.84	

+ Sample is inhomogeneous; values here are given as a guide as the actual composition is variable across the pellet

# Processing impurity

@ Composition varies from almost pure thoria to almost pure urania

\* Variable composition

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table H-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-16, Th/U-doped alkoxide-route and wet-milled oxide-route batches. Pellets were sintered in air at 1350°C for 4 hours.**

Sample No.	mws980280			mws980276		
	alkoxide			wet-milled oxide		
	<b>Pyr</b>	<b>Bran</b>	<b>Whit</b>	<b>Pyr</b>	<b>Bran</b>	<b>Whit</b>
<b>~ abundance (vol. %)</b>	60 - 70	20 - 30	10	60 - 65	25 - 30	10
<b>Element</b>						
<b>oxygen</b>	7	6	8	7	6	8
<b>Ca</b>	1.11	0.09	0.24	1.05	0.12	2.66
<b>Gd</b>	0.26	0.13	0.23	0.26	0.16	0.23
<b>Hf</b>	0.22	0.15	0.02	0.22	0.14	0.01
<b>U</b>	0.45	0.38	0.05	0.42	0.36	0.02
<b>Th</b>	0.17	0.34	0.02	0.17	0.34	0.03
<b>Ti</b>	1.91	1.99	0.18	1.95	1.98	0.09
<b>P</b>			1.82			1.87
<b>Mg<sup>#</sup></b>			0.12			
<b>Total</b>	4.12	3.08	4.88	4.09	3.10	4.92

# processing impurity

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table H-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-16, Th/U-doped alkoxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1300°C for 4 hours, 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980321			mws980307			mws980393		
	1300°C 4 h			1400°C 4 h			1375°C 75 h		
	Pyr	Bran	Whit + Matrix*	Pyr	Bran	Whit	Pyr	Bran	Whit
~ abundance (vol. %)	65 - 70	20 - 25	10	70	20	10	70	20	10
Element									
oxygen	7	6	8	7	6	8	7	6	8
Ca	1.00	0.09 – 0.14	2.21	0.96	0.06	2.64	0.94	0.05	2.65
Gd	0.23	0.12	0.17 <sup>\$</sup>	0.25	0.12	0.19	0.24	0.10	0.18
Hf	0.29	0.15	0.06 <sup>\$</sup>	0.29	0.15	0.01	0.29	0.16	0.001
U	0.40	0.39	0.12 <sup>\$</sup>	0.40	0.37	0.02	0.38	0.41	0.005
Th	0.18	0.32	0.09 <sup>\$</sup>	0.18	0.37	0.02	0.20	0.38	0.02
Ti	1.96	1.98	0.52 <sup>\$</sup>	1.97	1.99	0.07	1.98	1.96	0.02
P			1.56			1.92			2.01
<b>Total</b>	4.06	3.10	4.75	4.04	3.06	4.88	4.03	3.05	4.87

\* whitlockite grains are too small to analyse accurately, spectra contain overlaps from surrounding matrix material (brannerite and pyrochlore).

\$ EDS spectra emissions from surrounding matrix increase these elemental values.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table H-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-16, Th/U-doped oxide-route batches, wet-milled 16 hours. Pellets were sintered in Ar at 1400°C for 4 hours or 1350°C for 75 hours.**

Sample No.	mws980412				mws980398			
	1400°C 4 h				1350°C 75 h			
	Pyr	Bran	Whit	Oxide in Bran	Pyr	Bran	Whit	Oxide
~ abundance (vol. %)	70 - 75	15 - 20	10	< 1	70	20	10	0.5
<b>Element</b>								
<b>oxygen</b>	7	6	8	2	7	6	8	2
<b>Ca</b>	0.95	0.04	2.64	0.07	0.97	0.05	2.55	0.07
<b>Gd</b>	0.25	0.10	0.21	0.03	0.27	0.08	0.21	0.03
<b>Hf</b>	0.28	0.13	0.005	0.01	0.24	0.10	0.005	0.007
<b>U</b>	0.40	0.45	0.003	0.85	0.42	0.42	0.03	0.85
<b>Th</b>	0.19	0.36	0.02	0.03	0.21	0.42	0.03	0.04
<b>Ti</b>	1.96	1.97	0.02	0.06	1.95	1.96	0.07	0.06
<b>P</b>			1.99				1.95	
<b>Total</b>	4.04	3.05	4.89	1.04	4.05	3.04	4.84	1.04

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX I**

### **SCANNING ELECTRON MICROGRAPHS AND ENERGY DISPERSIVE X-RAY SPECTROMETRY RESULTS FOR THE PLUTONIUM-DOPED SAMPLES**

## I. APPENDIX I: SEM/EDS RESULTS FOR THE PLUTONIUM-DOPED SAMPLES

### KEY TO PHASE ABBREVIATIONS USED IN TABLES

Oxide	(U,Pu)O <sub>2</sub>
Bran	Pu/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Rutile	rutile (Hf-doped)
Per	perovskite
Whit	whitlockite

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table I-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-1, Pu/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	Pu92-01a (mws980293)				Pu67				Pu68				
	alkoxide				Dry-milled oxide				wet-milled oxide				
~ abundance (Vol. %)	Pyr	Bran	Rutile		Pyr	Bran	Rutile	Oxide		Pyr	Bran	Rutile	Oxide
	80	15	5		75-79	15-20	5	1		80	15	5	< 1
Element													
oxygen	7	6	2		7	6	2	2		7	6	2	2
Ca	1.01	0.09	0.001		0.90	0.05		0.06		0.99	0.08	0.001	0.11
Gd	0.23	0.13			0.19	0.09		0.03		0.24	0.14	0.002	0.08
Hf	0.23	0.12	0.08		0.26	0.15	0.10	0.03		0.22	0.11	0.08	0.03
U	0.42	0.54	0.007		0.43	0.60	0.01	0.40		0.41	0.53	0.009	0.42
Th	0.22	0.21	0.002		0.26	0.23		0.50		0.21	0.21	0.001	0.40
Ti	1.96	1.99	0.91		1.94	1.90	0.89			1.98	2.00	0.91	0.04
Al <sup>#</sup>					0.03	0.05		0.02					
Total	4.07	3.07	1.00		4.01	3.09	1.00	1.04		4.05	3.08	1.00	1.07

# processing impurity

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table I-2: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from the Task 12, Baseline plus impurities batches. Pellets were sintered in Ar at 1300 - 1325°C for 4 hours.**

Sample No.	Pu73					Pu75 (mws980200)					
Route	Alkoxide					Oxide					
Composition	B1-3 (A-9)					A-7					
Sintering Temp (°C)	1300					1325					
~ abundance (vol. %)	Pyr	2M Zirc	Bran	Rutile	Silicate <sup>§</sup>	Pyr	2M Zirc	Bran	Rutile	Oxide	Silicate <sup>§</sup> &
Element	75 - 80	7 - 10	10	3	1 - 2	70 - 75	10	10	5 - 7	< 1	1 - 2
oxygen	Wt. %					Wt. %					
Ca	0.91	0.65	0.07	2	13	0.98	0.76	0.10	2	0.13	2
Gd	0.17	0.19	0.13	0.09	1.7	0.25	0.17	0.17	0.003	0.07	
Hf	0.20	0.71	0.14	0.09	3.7	0.18	0.67	0.09	0.06	0.03	
U	0.43	0.15	0.56	0.01	5.4	0.43	0.16	0.50	0.01	0.43	
Pu	0.27	0.19	0.23	0.89	4.3	0.22	0.08	0.22	0.92	0.38	
Ti	1.87	1.63	1.90	11	11	1.97	0.04	1.99	0.92	0.05	
Mg	0.03	0.14	0.06	0.02	1.8	0.03	0.17	0.03	0.006		
Al	0.06	0.20	0.16	5.3	13	0.03	0.03	0.03			
Ga				0.1	5.3						
K				2.1	0.1						
Na				2.1	2.1						
Si				35	35						
Ta	0.07										
W											
Mo					0.6						
Ni											
Fe		0.02			0.4		0.06				
P					1.2						
B											
Cr											
Zn											
<b>Total</b>	4.01	4.04	3.09	1.01	100	4.06	4.01	3.10	1.00	1.08	

§ typical values  
 & too small to analyse  
 Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

Table I-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-9, Pu/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	Pu093-01a (mws980294)				Pu098-01a (mws980353)				Pu097-01a (mws980352)					
	alkoxide				Dry-milled oxide				wet-milled oxide					
~ abundance (Vol. %)	Pyr	2M Zirc	Bran	Rutile	Pyr	2M Zirc	Bran	Rutile	Oxide	Pyr	2M Zirc	Bran	Rutile	Oxide
Element	30 - 40	30 - 40	20	3	39 - 56	30 - 40	10 - 15	3 - 5	1	45 - 47	40	10	3 - 5	< 1
oxygen	7	7	6	2	7	7	6	2	2	7	7	6	2	2
Ca	0.99	0.82	0.08	0.002	0.94	0.83	0.06	0.11	0.004	0.95	0.83	0.05	0.11	0.004
Gd	0.23	0.16	0.12	0.10	0.24	0.14	0.14	0.008	0.009	0.22	0.15	0.13	0.008	0.014
Hf	0.27	0.75	0.13	0.009	0.29	0.77	0.13	0.008	0.009	0.28	0.76	0.15	0.008	0.014
U	0.37	0.11	0.50	0.001	0.37	0.10	0.43	0.007	0.009	0.36	0.10	0.47	0.001	0.014
Pu	0.25	0.08	0.25	0.85	0.27	0.07	0.33	0.88	0.95	0.28	0.08	0.27	0.88	0.91
Ti	1.94	1.86	1.99	0.01	1.93	1.86	1.95	0.01	0.04	1.94	1.89	1.97	0.01	0.07
Al		0.24				0.23	0.04				0.20	0.04		
<b>Total</b>	<b>4.05</b>	<b>4.01</b>	<b>3.07</b>	<b>1.00</b>	<b>4.03</b>	<b>4.00</b>	<b>3.07</b>	<b>1.00</b>	<b>1.00</b>	<b>4.03</b>	<b>4.00</b>	<b>3.07</b>	<b>1.00</b>	<b>1.00</b>

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table I-4: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-11, Pu/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.**

Sample No.	Pu094-01a (mws980295) alkoxide			Pu100-01a (mws980355) Dry-milled oxide			Pu099-01a (mws980354) wet-milled oxide			
~ abundance (vol. %)	Pyr 48 - 60	Bran 40 - 50	Oxide 2	Pyr 45 - 47	Bran 50	Rutile 3 - 5	Oxide < 1	Pyr 45 - 47	Bran 50	Rutile 3 - 5
Element										
oxygen	7	6	2	7	6	2	2	7	6	2
Ca	1.06	0.10	0.14	0.95	0.07			0.97	0.07	
Gd	0.24	0.15	0.11	0.23	0.13			0.22	0.12	
Hf	0.22	0.11	0.07	0.27	0.14	0.10	0.003	0.25	0.13	0.09
U	0.47	0.52	0.49	0.40	0.51	0.006	0.006	0.41	0.51	0.006
Pu	0.22	0.19	0.28	0.24	0.23	0.001	0.95	0.24	0.22	
Ti	1.89	2.02	0.006	1.94	1.99	0.89	0.04	1.96	2.01	0.90
<b>Total</b>	4.09	3.09	1.10	4.04	3.07	1.00	1.00	4.04	3.06	1.00

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system



Table I-6: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-15, Pu/U-doped alkoxide-route, dry milled oxide-route and wet-milled oxide-route batches. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	Pu106-01a (mws980362)					Pu104-01a (mws980359)					Pu103-01a (mws980358)					
	alkoxide					Dry-milled oxide					wet-milled oxide					
~ abundance (vol. %)	Pyr	Bran	Whit	Rutile		Pyr	Bran	Whit	Rutile	Oxide		Pyr	Bran	Whit	Rutile	Oxide &
Element	78 - 80	10	5 - 7	5		73 - 80	10 - 15	5 - 7	5	< 1		71 - 80	10 - 15	5 - 7	5 - 7	<< 1
oxygen	7	6	8	2		7	6	8	2	2		7	6	8	2	
Ca	0.90	0.06	2.61			0.94	0.06	2.63				0.96	0.05	2.62		
Gd	0.26	0.14	0.22			0.24	0.14	0.22				0.26	0.15	0.22		
Hf	0.21	0.11	0.005	0.07		0.24	0.13	0.007	0.09			0.23	0.12	0.006	0.09	
U	0.41	0.53		0.01		0.36	0.49	0.001	0.006	0.003		0.37	0.46	0.003	0.006	
Pu	0.26	0.23	0.02			0.31	0.25	0.02	0.001	0.98		0.26	0.29	0.02		
Ti	1.98	2.00	0.01	0.92		1.95	2.00	0.01	0.90	0.013		1.96	2.00	0.02	0.91	
P			2.00					1.98						1.98		
<b>Total</b>	4.02	3.06	4.86	1.00		4.03	3.07	4.87	1.00	1.00		4.05	3.06	4.87	1.00	

& grains too small to analyse

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

## **APPENDIX J**

### **SCANNING ELECTRON MICROGRAPHS AND ENERGY DISPERSIVE X-RAY SPECTROMETRY RESULTS OF SAMPLES SINTERED IN 3.7 % HYDROGEN IN ARGON**

**J. APPENDIX J: SEM/EDS RESULTS OF SAMPLES SINTERED IN 3.7 % HYDROGEN IN ARGON****KEY TO PHASE ABBREVIATIONS USED IN TABLES**

Oxide	(U,Th)O <sub>2</sub>
Bran	Th/U-brannerite
Pyr	pyrochlore
2M Zirc	2M zirconolite
4M Zirc	4M zirconolite
Per	perovskite

Note: the standard deviation on most of the EDS measurements is ~ 0.01 to 0.02 formula units. For elements present at < 0.01 formula units the standard deviation is typically in the range 20 – 50 %.

**Table J-1: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-2, Th/U-doped alkoxide-route batch. Pellets were sintered in 3.7 % H<sub>2</sub> in Ar at 1350°C for 4 hours.**

Sample No.	mws980297		
	<b>Pyr</b>	<b>2M Zirc</b>	<b>per</b>
~ abundance (vol. %)	70 - 75	15 - 20	10
<b>Element</b>			
<b>oxygen</b>	7	7	4
Ca	0.70	0.55	0.60
Gd	0.20	0.13	0.06
Hf	0.22	0.56	0.008
U	0.49	0.16	0.04
Th	0.23	0.08	0.08
Ti <sup>#</sup>	2.06	2.33	0.98
Na <sup>#</sup>			0.14
<b>Total<sup>*</sup></b>	<b>3.90</b>	<b>3.81</b>	<b>1.93</b>

# processing impurity, source unknown.

\* low "totals" are typical of Synroc samples formed severely reducing conditions, where the titanates contain Ti<sup>3+</sup>.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table J-2: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-10, Th/U-doped alkoxide-route batch. Pellets were sintered in 3.7 % H<sub>2</sub> in Ar at 1350°C for 4 hours.**

Sample No.	mws980299			
	Pyr	4M Zirc	2M Zirc	Per
~ abundance (vol. %)	30 - 35	30 - 35	30 - 35	2 - 3
Element				
oxygen	7	7	7	4
Ca	0.82	0.59	0.66	0.75
Gd	0.20	0.15	0.15	0.06
Hf	0.25	0.53	0.70	0.02
U	0.43	0.15	0.15	0.03
Th	0.26	0.11	0.09	0.06
Ti	1.99	2.16	1.99	0.94
Al	0.03	0.20	0.17	0.04
<b>Total *</b>	<b>3.97</b>	<b>3.88</b>	<b>3.91</b>	<b>1.90</b>

\* low "totals" are typical of Synroc samples formed severely reducing conditions, where the titanates contain Ti<sup>3+</sup>.  
 Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

**Table J-3: EDS analyses of phases (number of cations) in the pellets made from the Task 1.2, B1-12, Th/U-doped alkoxide-route batch. Pellets were sintered in 3.7 % H<sub>2</sub> in Ar at 1350°C for 4 hours.**

Sample No.	mws980301									
	<b>Pyr</b>	<b>Bran</b>	<b>Bran</b>	<b>Bran</b>	<b>Bran</b>	<b>Bran</b>	<b>4M Zirc</b>	<b>Oxide</b>		
		“bright zone”	“bright zone”	“dark zone”	“dark zone”					
~ abundance (vol. %)	65 - 70		10 - 15				10 - 15	2 - 3		
Element										
oxygen	7	6	6	6	6	6	7	2		
Ca	0.74	0.07	0.02	0.04	0.03	0.50	0.02			
Gd	0.23	0.04	0.03	0.06	0.05	0.19	0.03			
Hf	0.22	0.11	0.10	0.08	0.07	0.42	0.02			
U	0.54	0.55	0.53	0.37	0.36	0.23	0.53			
Th	0.21	0.33	0.38	0.25	0.24	0.09	0.33			
Ti	2.00	1.95	1.96	2.24	2.28	2.38	0.10			
<b>Total</b>	<b>3.93</b>	<b>3.05</b>	<b>3.02</b>	<b>3.04</b>	<b>3.03</b>	<b>3.80</b>	<b>1.02</b>			

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system